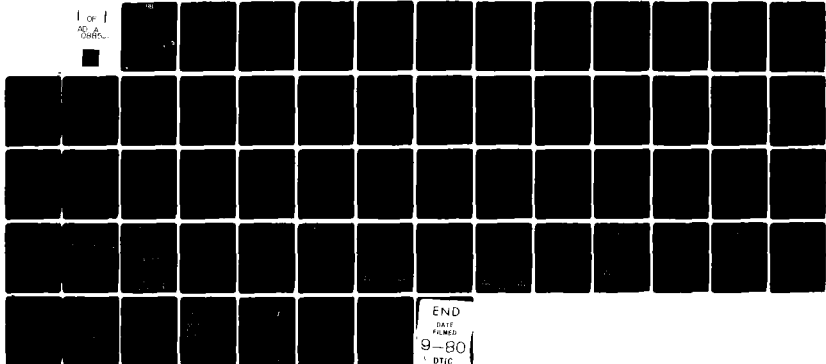


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"VIBRONIC ASSIGNMENTS AND VIBRONIC COUPLING  
IN THE  $^1E$  STATE OF SYM-TRIAZINE BY TWO PHOTON SPECTROSCOPY"

by

J. D. WEBB, K. M. SWIFT, and E. R. BERNSTEIN

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two photon photoacoustically detected spectra are reported for the first excited singlet state $^1E$ of sym-triazine in the gas phase. The origin has been positively identified as of $E$ symmetry through contour calculations and hot band observations. The excited state absorption is dominated by a highly irregular progression. These observations include: $6_0^1(A_1)$ $20\text{ cm}^{-1}$ .		

## I. INTRODUCTION

The molecular properties of sym-triazine ( $C_3N_3H_3$ ) have been of considerable continued interest over the past 25 years.<sup>1-16</sup> Optical spectroscopy has been one of the major ongoing efforts in the study of geometry, excited state energy levels, and dynamics of sym-triazine. There are a number of reasons for this. First, sym-triazine is of high molecular symmetry ( $D_{3h}$ ) with relatively few atoms, thereby reducing its vibrational and electronic complexity to some extent. Second, it is the only small aromatic molecular system with a degenerate, readily accessible, first excited state. Third, vibronic coupling in this system can be quite extensive; both intrastate (Jahn Teller - JT) and interstate (pseudo-Jahn Teller - PJT) couplings are potentially large. Fourth, the molecule is of considerable biological interest, particularly as a model system for many other nitrogen heterocycles. Fifth, radiationless relaxation from the lowest singlet and triplet states is fast and for the most part poorly understood. In view of the foregoing, it was thought that the new technique of two photon spectroscopy would be an excellent method for the further study of this system.

The first optical spectrum of triazine vapor located a broad, intense transition at 272 nm,<sup>1</sup> which was assigned by solvent shift studies as  $n \rightarrow \pi^*$  ( $A''_2$ ).<sup>2,4</sup> Subsequent analysis of the hot band region showed many of the weak, sharp features were associated with an electric dipole (one photon) forbidden  $E''$  state.<sup>8</sup> Low temperature crystal studies have confirmed these assignments.<sup>9-13</sup> Single vibronic level fluorescence (SVLF) spectra are also in agreement with this conclusion.<sup>14</sup>

The  ${}^1E'' \leftarrow {}^1A'_1$  transition is two photon allowed and it was felt two photon spectroscopic experiments would be an obvious way to

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20. ABSTRACT (continued)

$6_0^1(E'')$   $\sim 227 \text{ cm}^{-1}$ ,  $6_0^2(E'')$   $\sim 556 \text{ cm}^{-1}$ ,  $6_0^3(E'')$   $\sim 693 \text{ cm}^{-1}$ , and possibly  $6_0^4(E'')$  [ $8_0^1(E'')$  or  $19_0^1(E'')$ ]  $\sim 836 \text{ cm}^{-1}$  above the  $^1E''$  origin. The one photon observed  $6_0^1(A_2'')$  and  $6_0^2(A_2'')$  bands at  $677 \text{ cm}^{-1}$  and  $1176 \text{ cm}^{-1}$  respectively, fit in well with these assignments. These observations are strongly supported by a Jahn Teller calculation which predicts: little coupling between the  $A_2''$  and  $E''$  electronic manifolds; a large quadratic coupling and a small linear coupling in the  $E''$  manifold; and a quenched angular momentum in this state. Good agreement is shown to exist between one photon and two photon spectroscopic observations and the calculations.

$A_2'$

$E'$

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increase our understanding of the excited state, its geometry, vibronic coupling, and relaxation processes. However, since triazine is known to emit only weakly, two photon excitation experiments employing conventional detection techniques (fluorescence) were not expected to be successful. Photoacoustic detection does, however, provide a straightforward, reliable method for obtaining the desired gas phase spectra. We have recently reported preliminary results of two photon experiments on triazine detected by means of the photoacoustic effect and by fluorescence from photochemically generated cyanide (CN).<sup>17</sup> This paper presents more complete results and a more detailed discussion of our findings and conclusions. (It should be noted that some of the previous assignments have been changed in the present paper due to new experimental and theoretical findings but that the general conclusions remain unaltered.)

Vibronic assignments are made with the help of rotational contour analysis and polarization studies.<sup>18,19</sup> The isotropic part of the Q branch of a totally symmetric vibronic state will be observed in absorption if viewed in linearly polarized light but will not be observed if circularly polarized light is employed. The polarization behavior of hot bands can be used to imply the vibronic symmetry of the corresponding cold bands (Sect. IV). With these methods, combined with other standard techniques of spectroscopic analysis, it has been possible to give a unique assignment for most of the major features of the  ${}^1E'' \leftarrow {}^1A_1'$  absorption spectrum.

The presentation is organized as follows. In Section II we present background information on triazine and Jahn Teller (JT) coupling. Section III describes experimental details of the two photon photoacoustic and fluorescence apparatus employed. In Section IV we present experimental results. Rotational contour and vibronic coupling calculations used to

understand the spectroscopic assignments are given in Section V. Manifestations of the JT effect in the  ${}^1E''$  state are discussed in Section VI. Our findings are summarized in Section VII.

## II. BACKGROUND

Early spectroscopic studies of sym-triazine<sup>1,2,4</sup> suggested the energy level diagram and excited state symmetries shown in Figure 1. The intense portion of the 272 nm band observed in one photon spectra is seen to be the one photon allowed  $A_2''$  electronic state. However, Brinen's identification of the electronic origin was subsequently shown to be incorrect.<sup>4,8</sup> Ground state vibrational frequencies and rotational constants were determined by infrared and Raman spectroscopy<sup>3,5</sup>; these are given in Table I. Ground state geometry was determined to be planar, and of  $D_{3h}$  symmetry.

Udagawa's partial rotational contour analysis of one of the weak, sharp bands on the low energy side of the 272 nm band indicated that triazine is planar (or at least nearly so) in its lowest excited singlet state.<sup>7</sup> Fisher and Small were able to assign some of the sharp, weak transitions on the low energy side of the 272 nm band as being due to an  $E''$  electronic state by consideration of vibronic selection rules and by identification of some vibronically allowed hot bands.<sup>8</sup> They realized that JT coupling within the  $E''$  manifold was possible but they were unable to find definitive evidence for it. A summary of their vibrational assignments is given in Table II.

Knight and Parmenter's SVLF data<sup>14</sup> on sym-triazine support these  $E''$  electronic and  $6\frac{1}{0}$  ( $A_2''$ ) vibronic assignments. Only  $\nu_6$  appears to be active in the SVLF spectra, indicating that a model in which a single vibrational mode vibronically couples to the  $E''$  electronic state is reasonable. This situation is to be contrasted to that found for benzene<sup>20</sup> and transition metal hexafluorides.<sup>21-23</sup> Furthermore, the SVLF intensity pattern for the



$\nu_6$  progression [ $I(6_2^1) > I(6_4^1) \gg I(6_3^1) \sim I(6_5^1) \sim I(6_6^1)$ ] indicates that quadratic JT (QJT) coupling is more important than linear JT (LJT) coupling. If LJT vibronic coupling is dominant, the pumped level [the  $n=1$   $\nu_6(A_2'')$  vibronic component in the  ${}^1E''$  excited state] will be mixed with all other  $\nu_6(A_2'')$  components ( $n \geq 2$ ) in the  ${}^1E''$  electronic state, since LJT coupling has the selection rule  $\Delta n = \pm 1$ . In order for emission to occur, the electric dipole allowed  ${}^1A_2''$  electronic state about  $1500 \text{ cm}^{-1}$  above the  ${}^1E''$  origin must be mixed into the pumped level as well. LPJT coupling will mix  $\nu_6(A_2'')$  components ( $n = 0, 2, 3, \dots$ ) of the  ${}^1A_2''$  electronic state into the pumped level with the selection rule  $\Delta n = \pm 1$ . Since the pumped level has contained in it all  $\nu_6(A_2'')$  levels of the  ${}^1E''$  electronic state (due to LJT coupling), LPJT coupling will mix in all  $\nu_6(A_2'')$  components of the  ${}^1A_2''$  electronic state to some extent. Note that this coupling omits  $\nu_6$   $n = 1$  of  ${}^1A_2''$  which is of  $E''$  vibronic symmetry. QJT coupling, on the other hand, will mix  $\nu_6$  components of the  ${}^1E''$  electronic state according to the selection rule  $\Delta n = 0, \pm 2$ . Thus, the  $n = 1$   $\nu_6(A_2'')$  level which is being pumped will contain the other  $\nu_6(A_2'')$  components of the  ${}^1E''$  electronic state with odd  $n$ . LPJT coupling will mix in even  $\nu_6(A_2'')$  components from the  ${}^1A_2''$  electronic state according to the LPJT selection rule  $\Delta n = \pm 1$ . The intensity of the emission progression  $6_n^1(A_2'') ({}^1E'' \rightarrow {}^1A_1')$  will be proportional to  $\langle {}^1A_2'' n' | \underline{r} | {}^1A_1' n \rangle = \langle {}^1A_2'' | \underline{r} | {}^1A_1' \rangle \langle n' | n \rangle$  which, in the absence of large Franck-Condon shifts, will be greatest for  $n' = n$ . With LJT coupling mixing  $n = 0, 2, 3, 4, \dots$   $\nu_6(A_2'')$  levels of the  ${}^1A_2''$  electronic state into the pumped level, emission should occur to  $\nu_6$  levels  $n = 0, 2, 3, 4, \dots$  of the ground state. With QJT coupling dominant, the pumped level contains only even  $n$   $\nu_6(A_2'')$  components from the  ${}^1A_2''$  electronic state, so emission will occur to even  $n$   $\nu_6$  levels in the ground electronic state, thus predicting  $I(6_3^1) \sim 0$  and  $I(6_4^1)$  large in agreement with the experimental SVLF data. Figure 2 illustrates this effect and how it comes about.

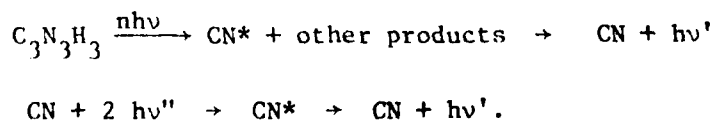
Barnard has carried out high resolution one photon studies of sym-triazine vapor and has done a careful rotational contour analysis.<sup>24</sup> He concluded that electronic angular momentum in the  ${}^1E''$  state is largely quenched ( $-0.2 < \zeta_e < 0.1$ ). A summary of his other results is included in Table II. An important conclusion from this work is that the  $6_0^2 (A''_2)$  state is only  $499 \text{ cm}^{-1}$  above the  $6_0^1 (A''_2)$  at  $677 \text{ cm}^{-1}$ . Such an energy level pattern is predicted by QJT calculations but never by LJT calculations.

The above discussion intimates that the QJT vibronic coupling is important in the  $E''$  electronic state of sym-triazine. Previous theoretical investigations of a QJT coupling have shown that it can be more influential in a given circumstance than might be obvious intuitively.<sup>21-23</sup> Some vibronic levels are effected by QJT coupling in first order perturbation theory whereas LJT coupling effects vibronic levels only in second order perturbation theory. A large quadratic JT effect is present in  $\text{ReF}_6$ <sup>21</sup> and  $\text{IrF}_6$ <sup>22</sup>. In addition, calculations for these molecules which allowed simultaneous JT coupling in two modes led to quite different results than if the two modes were considered separately.

### III. EXPERIMENTAL

Synthesis of  $\text{h}_3$ - and  $\text{d}_3$ - sym-triazine samples used in this study is described in references 13 and 25. Additional purification steps such as vacuum distillation, fusion with potassium, and distillation through molecular sieve were carried out in a grease-free vacuum system.

Initial two photon photoacoustic experiments were performed in a sample cell with windows sealed with lightly greased O-rings. It was found that HCN appeared as a decomposition product in such a cell. HCN evolution was monitored photoacoustically (one photon absorption) by observing the fifth overtone of the carbon-hydrogen stretch ( $\nu_3 = 3312 \text{ cm}^{-1}$  and  $5\nu_3 = 15552 \text{ cm}^{-1}$ ) which appears fortuitously in the midst of the two photon triazine spectrum. Subsequently, all two photon gas phase cells had windows sealed with indium gaskets; to the limit of our detection ability no HCN is produced in these new cells. However, decomposition is a problem in these experiments nonetheless, as triazine is apparently photodecomposed by an n photon process that is, in any event, two photon resonant. This photochemical process yields CN radicals. CN is detected photoelectrically by monitoring  $\text{B} \rightarrow \text{X}$  emission in the near ultraviolet, as cyanyl is produced in its excited state. CN is also observed in two photon absorption  $\text{B} \leftarrow \text{X}$  followed by emission. The overall process for this photochemistry is described as follows:



of two photon absorption is not observed photoacoustically, due either to high quantum yield for emission or low concentration of total photo-products. CN production involves a two photon resonant triazine process and, with the exception of the readily identified CN absorption ( $B(v=3) \leftarrow X$ ), CN fluorescence gives the same triazine line shapes and positions as does the photoacoustically detected spectrum. Some variations in relative intensities of vibronic features have been previously noted,<sup>17</sup> however.

All features observed in the two photon photoacoustically detected spectrum are due only to sym-triazine. This is confirmed by the existence of hot bands separated from cold bands by triazine ground state frequencies. Also, the  $d_3$ - triazine origin is blue-shifted by over  $100\text{ cm}^{-1}$  while most of the vibrational intervals are almost unchanged.

The experimental arrangement of the two photon photoacoustic apparatus is depicted in Fig.3. The tunable laser for these experiments is a Nd/YAG pumped dye laser (Quanta-Ray DCR-1 & PDL) with an output of 2MWatts over the range  $6200\text{--}6600\text{ \AA}$  using DCM dye. The laser beam is focused in front of a 1" condenser microphone (B&K 4145) mounted in a high vacuum stainless steel cell. A unique feature of this cell design is that a Teflon cup has been mounted on the microphone body in order to enhance signals and reduce background; the best signal occurs for the situation in which the distance between the microphone diaphragm and the end plate of the cup is as small as possible. Apparently two factors are important: focus should be as close to the diaphragm as possible, and the shock wave reflected from the cup should reach the diaphragm while it is still deformed from the initial shock wave. This latter situation insures better signal integration.<sup>26</sup>

Other important cell design features are: absence of grease or epoxy; metal (Cu) flange seals and indium window seals; metal-ceramic feedthrough

for microphone electrical connections; and Brewster output window of glass-blown quartz and molybdenum sealed. The angled output window eliminates background signals from reflected laser light impinging on the microphone assembly. An angled input window is less necessary and makes polarization experiments difficult.

The microphone signal is amplified (PAR 114/118 amplifier) and is processed by a boxcar integrator (PAR 164/162) (Channel A). The laser power level is monitored by a pyroelectric power meter (Molelectron) and processed in the second (B) channel of the boxcar. The two signals are subsequently ratioed ( $A/B^2$ ) to compensate for pulse-to-pulse variations and the power curve of the dye laser. Wavelength calibration is achieved by splitting off a small fraction of the dye laser beam and using the optogalvanic effect in a standard Fe-Ne hollow cathode lamp to observe well known atomic resonances. Circularly polarized light was produced in a Fresnel rhomb. Hot band experiments were performed at 100°C by heating the cell with a heating tape. Signal to noise ratio for these experiments was about a factor of two to three lower than for room temperature experiments due to depleted ground state population, convection currents in the cell, and increased microphone noise.

Two photon emission excitation experiments were also attempted (both fluorescence and phosphorescence). The experimental arrangement is similar to the above except a photomultiplier tube (RCA 8850) with appropriate filters was used as a detector. Pulses from the 8850 were fed into the boxcar integrator directly. At 10 Torr of sym-triazine vapor, no triazine emission was detected. However, emission from CN was observed, as previously described, and since it is two photon triazine resonant, the absorption could be followed with the  $B \rightarrow X$  CN emission. Even at 0.1 Torr only weak CN emission could be detected from the sample.

#### IV. EXPERIMENTAL RESULTS

Two photon photoacoustic spectroscopic data for  $h_3$ - and  $d_3$ -triazine are found in Table III and representative survey spectra and individual band contours can be found in Figures 4-9. The first step in assigning the spectrum is to determine the excited state vibronic symmetry for each of the bands. Rotational contour simulation can often associate a unique  $\Delta K$  selection rule with a given contour, which immediately gives the vibronic symmetry (see Table IV).<sup>27</sup> This method gives the symmetry of the lowest energy cold band as  $E''$ . Such an assignment is supported by the presence of a polarized hot band at  $-346\text{ cm}^{-1}$ . This frequency is close to the ground state value for  $\nu_{16}''(e'')$ . The transition assignment  ${}^1E'' \leftarrow {}^1E''$  ( $e'' {}^1A_1'$ ) ( $16_1^0$ ) explains both the location and polarization behavior of the band (Table IV). The lowest cold band is thus identified as an  $E''$  origin. The  $556\text{ cm}^{-1}$ ,  $693\text{ cm}^{-1}$ ,  $836\text{ cm}^{-1}$  and  $1071\text{ cm}^{-1}$  features are assigned in a similar manner as  $E''$  vibronic states. The  $210\text{ cm}^{-1}$  band (see Fig.8) does not have an easily recognizable  $E''$  rotational contour (vide infra), but it may be assigned as  $E''$  with confidence, since its  $\nu_{16}''$  hot band is polarized and an  $E''$  contour can be calculated for it. An  $A_1'$  band is observed at  $436\text{ cm}^{-1}$  by its polarization behavior. No  $E'$  contours are identified.

It is somewhat more difficult to determine the vibrational parentage of each transition. The  $A_1'$  band at  $436\text{ cm}^{-1}$  must be due to an  $e''$  vibration, since only  $e'' \times E''$  contains  $A_1'$  in  $D_{3h}$ . It is thus either  $16_0^1(A_1')$  or  $10_0^1(A_1')$ . Since it has a small isotope shift,  $10_0^1(A_1')$ , an out of plane hydrogen bending motion, can be ruled out. Also, the  $\nu_{16}''$  hot band of this transition is unusually intense, implying that it is a sequence band ( $16_1^1$ ). The weaker polarized feature at  $445\text{ cm}^{-1}$  in  $h_3$  spectra is not a hot band and

is tentatively assigned as  $10_0^1 (A_2')$ . Since it does not evidence a  $10_1^1$  sequence band ca.  $-585 \text{ cm}^{-1}$  and a comparable set of features is not located in  $d_3$  spectra, this assignment remains less certain than  $16_0^1 (A_1')$ . It should be noted that both these values ( $436$  and  $445 \text{ cm}^{-1}$ ) are quite different from those reported in Table II based on one photon results. However, both  $\nu_{10}$  and  $\nu_{16}$  are  $e''$  modes with vibronic components  $A_1'$  (two photon allowed),  $A_2'$  (forbidden), and  $E'$  (one photon allowed); thus the two experiments observe different vibronic components. In this work we have not analyzed the cause of this splitting but it must arise from either anharmonicities leading to  $\nu_{16}-\nu_{10}$  coupling, quadratic intrastate vibronic coupling, or strong Herzberg-Teller coupling with  $E'$ ,  $A_1'$ , or  $A_2'$  electronic states. It would certainly be interesting to pursue the causes of these vibronic splittings.

The totally symmetric vibration  $12_0^1(E'')$  is identified by its known frequency<sup>8</sup>, its similarity in line shape and structure to the origin, and by the non-totally symmetric modes built on it. Most of the remaining bands in the region below  $(0,0) + 1000 \text{ cm}^{-1}$  are of  $E''$  vibronic symmetry and could be of  $a_1'$ ,  $a_2'$ , or  $e'$  vibrational parentage. We rule out the  $a_1'$  totally symmetric vibrations since no Franck Condon progressions are observed and non-totally symmetric vibrations are not built on any of these features. Since isotope shifts are small for these low lying modes,  $\nu_3'$ ,  $\nu_{20}'$ , and  $\nu_9'$  may be eliminated as candidates. The ground state frequency of  $\nu_{14}$  is too high and it can only appear via Herzberg-Teller coupling which would not be capable of producing the observed intensity. The only remaining vibrational assignments for the four  $E''$  bands below  $(0,0) + 1000 \text{ cm}^{-1}$  are  $\nu_8'$ ,  $\nu_{19}'$ , and  $\nu_6'$ . Since in the one photon vibronically allowed spectrum,  $6_0^1 (A_2'')$  has been assigned at  $677 \text{ cm}^{-1}$  we can assume that  $\nu_6'$  is the lowest energy of the  $e'$  excited state modes;  $8_0^1 (A_2'')$  and  $19_0^1 (A_2'')$  appear to be over  $1000 \text{ cm}^{-1}$  (Table II) from the origin. Thus the two lowest  $E''$  bands ( $210$  and  $556 \text{ cm}^{-1}$ ) are assigned as

components of  $\nu_6^1$  ( $6_0^1$  (E'') and  $6_0^2$  (E'')), respectively. The unusual assignment of  $6_0^1$  (E'') at  $210 \text{ cm}^{-1}$  is supported by the presence of a relatively intense sequence hot band  $6_1^1$  (E'') at  $-476 \text{ cm}^{-1}$ . From these arguments it is not obvious how the remaining two E'' features below  $(0,0) + 1000 \text{ cm}^{-1}$  should be labeled and we defer this discussion until Section VI.

Finally, the origin region will be discussed at greater length. An unusual feature appears at  $-24 \text{ cm}^{-1}$ , as shown in Figure 5, which is not reproduced in rotational contour calculations of the E'' origin.

The most obvious assignment is  $16_1^1$  (E') but there are a number of observations which tend to contradict this assignment. The  $-24 \text{ cm}^{-1}$  peak does not appear to increase enough in intensity upon heating to  $100^\circ\text{C}$  to be  $16_1^1$  (E'), but overlap with the origin contour and poor signal to noise ratio at  $100^\circ\text{C}$  make this result inconclusive. Moreover, such a feature is not observed to be associated with other E'' contours (see Figures 5-8) and one would expect analogous sequence structure to appear on every feature of appropriate symmetry (i.e.,  $6_0^1$   $16_1^1$  (E') and  $6_0^2$   $16_1^1$  (E')). It should be noted that  $6_0^1$   $16_1^1$  (A'\_1) and  $6_0^2$   $16_1^1$  (A'\_1) are observed. That such a feature is indeed missing on the other E'' contours is confirmed by the fact that a  $\nu_6''$  hot band of the  $-24 \text{ cm}^{-1}$  peak is easily observed, whereas no  $\nu_6''$  hot bands of the missing  $6_0^1$   $16_1^1$  (E') and  $6_0^2$   $16_1^1$  (E') can be seen. A feature analogous to the  $-24 \text{ cm}^{-1}$  one does appear on the contour of the first totally symmetric built on the origin,  $12_0^1$  (E''). The  $\nu_6''$  hot band built on the  $-24 \text{ cm}^{-1}$  feature is in fact more intense than  $6_1^0$  (E''), indicating that it might be of the sequence type, namely  $6_1^1$  (A''\_1). This suggests that the  $-24 \text{ cm}^{-1}$  feature could be related to the presence of  $\nu_6^1$  (A''\_1) at the origin. How such a transition could obtain intensity is unclear, but since it is so near an intense feature, many perturbation mechanisms could be envisioned. Further discussion of this feature is postponed until JT calculations are discussed. J. Parkin has communicated to us that the one photon spectrum may also evidence an A''\_1 feature "below the E'' origin."



## V. CALCULATIONS

### A. $(E'' + A_2'')$ x $e'$ vibronic coupling.

General methods for vibronic coupling calculations may be found in references 21-23. A brief outline of the calculation is given here. We wish to emphasize that in spite of the differences between  $MF_6$  and triazine, the overall methods and even the results are quite similar.

The two lowest excited states of sym-triazine are energetically close ( $\sim 1500 \text{ cm}^{-1}$ ); thus vibronic coupling calculations should include not only vibronic coupling within the  $E''$  manifold, but also between  $E''$  and  $A_2''$  manifolds. The Hamiltonian includes both LJT and QJT terms between  $E''$  components but only linear terms between  $E''$  and  $A_2''$  components.

Since large matrices are diagonalized numerically, it is important to choose a basis set and phase convention which guarantees real matrix elements. Lax's convention seems most convenient for this purpose.<sup>28</sup>

$D_{3h}$  basis functions, matrix representations, and Clebsch-Gordon coefficients are then defined. A vibronic coupling matrix Hamiltonian appropriate for the  $(E'' + A_2'')$  manifold is formed in the usual fashion utilizing the Wigner-Eckart theorem to reduce the number of independent parameters to the minimum determined by symmetry:  $D$  is the LJT parameter;  $Q[a_1']$  and  $Q[e']$  are the QJT parameters;  $D'$  is the LPJT parameter which gauges the vibronic interaction between the  $E''$  and  $A_2''$  manifolds, and  $\Delta E$  is their separation. Next, a symmetry-adapted vibronic basis is formed. The first step is to determine appropriate combinations of two-dimensional harmonic oscillator functions of the usual polar coordinate type which transform according to the irreducible representations of  $D_{3h}$ . These may then be combined with electronic factors using Clebsch-Gordon coefficients. Secular energy matrices are formed by taking matrix

elements of the symmetry adapted basis functions with the matrix Hamiltonian. Separate  $E''$ ,  $A_2''$ ,  $A_1''$  blocks are thereby formed. General formulae for the matrix elements of harmonic oscillator function with powers of vibrational coordinates are available.<sup>29</sup> We have used a basis formed from all appropriate harmonic oscillator functions up to  $n = 20$ . Details of this calculation are given in the appendix.

Examples of these calculations are given in Figures 10 and 11 and Table V. In Figure 10, the effect of LPJT coupling is illustrated; in Figure 11 the regime of large QJT coupling with only a small LJT parameter is explored. These calculations will be compared with the experimental findings in Section VI. Table V provides precise numerical data which will allow comparison with other calculations.

#### B. Rotational Contour Calculations.

The rotational contour calculations were carried out in the usual manner.<sup>19,30-32</sup> Sym-triazine nuclear statistical weights were employed but seem to make little difference in the contours at the resolution used ( $0.5 \text{ cm}^{-1}$ ). The quantum number  $J$  was varied from 0 to 100. No line shape function was used for the individual transitions; all intensity was placed in a box covering  $0.5 \text{ cm}^{-1}$  and the points thus generated were connected with lines on a computer plotter.

## VI. JAHN TELLER INTERPRETATION OF THE $\nu_6'$ MODE

The behavior of  $\nu_6$  in the E'' electronic state of sym-triazine is clearly highly unusual: large energy differences between  $6_0^1$  (A'') and  $6_0^1$  (E''); an anharmonic  $\nu_6$  progression; and many E'' modes within a  $1000\text{ cm}^{-1}$  of the E'' origin. Reasons for this abnormal behavior are discussed in this section.

The electronic degeneracy of the E'' electronic state and the proximity of an A''<sub>2</sub> electronic ( $\sim 1000\text{ cm}^{-1}$ ) state strongly suggest that some form of vibronic interaction (JT or PJT) is responsible for the highly irregular nature of  $\nu_6'$  bands.

It is immediately clear upon examining Figure 10 that PJT interaction between E'' and A''<sub>2</sub> electronic states is not responsible for the observed  $\nu_6'$  behavior since it places the E''  $\nu_6$  vibronic components above the A''<sub>2</sub>  $\nu_6$  components. Experimentally, the lowest E''  $\nu_6'$  is observed at  $210\text{ cm}^{-1}$ , and one photon experiments place the A''<sub>2</sub> ( $6_0^1$ ) at  $677\text{ cm}^{-1}$ . Table VI shows that there is, however, a set of parameters for the JT calculation which qualitatively accounts for the observed  $\nu_6'$  bands. In fact, the  $693\text{ cm}^{-1}$  band which is not assigned in Section IV fits well as  $6_0^3$  (E'') and indeed is predicted to have considerable intensity. Based on these calculations,  $6_0^4$  is most likely assigned as the  $836\text{ cm}^{-1}$  (E'') feature (see Table III for other possibilities, however). Strength of the  $n\nu_6$  series interpretation is evidenced by the fact that six energy levels are approximately calculated with only two parameters (see Table VI). The calculation also reproduces the observations that A''<sub>2</sub> levels in the  $0\text{--}1500\text{ cm}^{-1}$  region above the origin are sparse, and that there are many E'' levels in the  $0\text{--}1500\text{ cm}^{-1}$  range. Moreover, an A''<sub>1</sub> comes into near coincidence with the origin, in agreement with the perturbed origin contour.

The small coriolis coupling constant obtained from the rotational contour analysis of the E" origin (Section VB) supports the above interpretation since JT vibronic coupling is expected to quench electronic angular momentum. Further evidence for a substantial JT effect in the  $\nu_6^1$  progression is apparent from the variation of the moments of inertia for triazine in the  $n\nu_6^1$  vibronic states; these are respectively for  $n=0$  to 3, .2126, .2172, .2126, and .2121.

Calculated intensity patterns for  $6_n^1$  ( $A_2''$ ) emission do not agree well with the observed ones as reported in SVLF studies.<sup>14,15</sup> Inspection of the  $\nu_6^1$  ( $A_2''$ )  $677\text{ cm}^{-1}$  eigenvector calculated with parameters D, D', Q[e'], and  $\nu^0$  given in Table VI, shows I ( $6_3^1$ ) larger than observed relative to I ( $6_2^1$ ) and I ( $6_4^2$ ). The proximity of  $6_0^1$  ( $A_2''$ ) at  $677\text{ cm}^{-1}$  and  $6_0^3$  ( $E''$ ) at  $693\text{ cm}^{-1}$  may perturb the observed pattern, however. It is not unreasonable to expect only qualitative agreement here since several approximations have been made. Improvements might be realized by including cubic terms or simultaneous JT coupling with other e' vibrational modes (e.g.,  $\nu_8^1$ ).<sup>22</sup> Certainly extensive Herzberg-Teller couplings are to be expected for this system and have been largely ignored in the calculation.

While substantial JT coupling in the E" electronic manifold is probably to be expected, it is however counter-intuitive that the QJT parameter Q[e'] is greater than the LJT parameter D. It may be that there is some "hidden" or approximate symmetry present in sym-triazine which tends to minimize LJT coupling. For example, many of the molecular orbitals of sym-triazine possess near cylindrical symmetry. Since  $\nu_6^1$  is an in-plane vibration, the entire electronic and vibrational coupling may mimic the cylindrical symmetry of a linear molecule; it is well known that LJT terms are zero for linear molecules (the Renner Teller Effect).

## VII. CONCLUSIONS

Two photon photoacoustic spectra of the lowest excited state  $^1E''$  of sym-triazine have been obtained. The electronic symmetry has been shown to be  $E''$  by direct observation of rotational contours of the origin band and by observation of hot bands associated with this origin. Electronic angular momentum of this state is quenched ( $\zeta_e \sim 0.1$ ).  $\nu_6'$  vibronic components dominate the remainder of the spectrum from 0-1500  $\text{cm}^{-1}$  and possess highly irregular intervals. Large splittings exist between  $A_1''$ ,  $A_2''$ , and  $E''$  vibronic  $\nu_6'$  components.

It has been possible to fit and explain such an unusual progression for  $\nu_6'$  based on a vibronic coupling calculation which has QJT coupling terms  $Q[e']$  larger by a factor of four than LJT coupling terms  $D$ . PJT coupling with the nearby  $A_2''$  state appears not to be important for this energy level scheme.

The two photon photoacoustic experimental technique has been demonstrated to be a sensitive method for obtaining the data. It is complementary to fluorescence excitation detection techniques. Through the use of photoacoustic detection, interference of CN photochemiluminescence was eliminated. The CN emission did, however, reproduce the photoacoustic spectrum in all essential features.

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REFERENCES

1. C. Grundmann, A. Kreutzberger, J. Am. Chem. Soc. 76, 632 (1954).
2. R. C. Hirt, F. Halverson, R. G. Schmitt, J. Chem. Phys. 22, 1148 (1954).
3. J. E. Lancaster, N. B. Colthup, J. Chem. Phys. 22, 1149 (1954).
4. J. S. Brinen, L. Goodman, J. Chem. Phys. 31, 482 (1959); 35, 1219 (1961).
5. J. E. Lancaster, R. F. Stamm, N. B. Colthup, Spectrochem. Acta 17, 155 (1961).
6. K. K. Innes, J. P. Byrne, I. G. Ross, J. Mol. Spec. 22, 125 (1967).
7. Y. Udagawa, M. Ito, S. Nagakura, J. Mol. Spec. 39, 400 (1971).
8. G. Fischer, G. J. Small, J. Chem. Phys. 56, 5934 (1972).
9. R. M. Hochstrasser, A. H. Zewail, Chem. Phys. Lett. 11, 157 (1971); J. Chem. Phys. 55, 5291 (1971).
10. R. M. Hochstrasser, Chem. Phys. Lett. 17, 1 (1972).
11. R. M. Hochstrasser, T. S. Lin, A. H. Zewail, J. Chem. Phys. 56, 637 (1972).
12. T. J. Aartsma, D. A. Wiersma, Chem. Phys. 1, 211 (1973).
13. E. R. Bernstein, R. E. Smalley, J. Chem. Phys. 58, 2197 (1973); Chem. Phys. 2, 321 (1973).
14. A. E. W. Knight, C. S. Parmenter, Chem. Phys. 43, 257 (1979).
15. A. E. W. Knight, C. S. Parmenter, Chem. Phys. 15, 85 (1976).
16. P. R. Nott, B. K. Selinger, Aust. J. Chem. 31, 1889 (1978).
17. J. D. Webb, K. M. Swift, E. R. Bernstein, J. Mol. Structure 61, 285 (1980).
18. J. H. Callomon, T. M. Dunn, I. M. Mills, Philos. Trans. R. Soc. London Ser. A.259, 499 (1965).
19. F. Metz, W. E. Howard, L. Wunsch, H. J. Neusser, E. W. Schlag, Proc. Roy. Soc. London A363, 381 (1978).

20. J. van Egmond, J. H. van der Waals, Mol. Phys. 28, 457 (1974).
21. G. R. Meredith, J. D. Webb, E. R. Bernstein, Mol. Phys. 34, 995 (1977).
22. E. R. Bernstein, J. D. Webb, Mol. Phys. 37, 191 (1979).
23. E. R. Bernstein, J. D. Webb, Mol. Phys. 36, 1113 (1978).
24. J. Barnard, Ph.D. Thesis, University College, London (1974).
25. R. E. Smalley, Ph.D. Thesis, Princeton University (1973).
26. J. J. Barrett, Private Communication.
27. K. M. Chen, E. S. Yeung, J. Chem. Phys. 69, 43 (1978).
28. M. Lax, Symmetry Principles in Solid State and Molecular Physics, Wiley-Interscience, New York (1974).
29. C. DiLauro, J. Mol. Spec. 41, 598 (1972).
30. W. Martin McClain, Robert A. Harris, Excited States, Volume 3, Ed. E.C. Lim, Academic Press, NY (1977), p. 1-56.
31. L. Wunsch, F. Metz, H. J. Nuesser, E. W. Schlag, J. Chem. Phys. 66, 386 (1977).
32. J. R. Lombardi, R. Wallenstein, T. W. Hänsch, D. M. Friedrich, J. Chem. Phys. 65, 2357 (1976).



TABLE 1. Ground state vibrations of sym-triazine.

Symmetry Type	Predominant Motion of Mode	Lord Numbering <sup>(a)</sup>	Frequency (cm <sup>-1</sup> ) <sup>(b)</sup>	
			$h_3$	$d_3$
$a_1'$	Hydrogen stretch	2	3042	2293
	In-plane ring bend	12	1132	1077
	Ring stretch	1	992	987
$a_2'$	Ring stretch	14	1617	1586
	In-plane hydrogen bend	3 or 15	1251	951
$e'$	In-plane hydrogen bend	20	3056	2280
	Ring stretch	8	1556	1530
	Ring stretch	19	1410	1284
	In-plane hydrogen bend	9	1174	931
	In-plane ring bend	6	675	662
$a_2''$	Out-of-plane ring bend	5	925	861
	Out-of-plane ring bend	4	737	577
$e''$	Out-of-plane hydrogen bend	10	1031	846
	Out-of-plane ring bend	16	340	309

Ground State Rotational Constants (cm<sup>-1</sup>)<sup>(c)</sup>

$$h_3 = .2146$$

$$d_3 = .19358$$

- a. R. C. Lord, A. L. Marston, F. A. Miller, Spectrochim. Acta 9, 113 (1957).  
 b. Reference 5.  
 c. J. E. Lancaster, B. P. Stoicheff, Can. J. Phys. 34, 1016 (1956).

TABLE 2. Electronic Origins and Vibrational Analysis of the  $1E''$  State  
Determined from One-Photon Spectra.

Electronic Origin (cm <sup>-1</sup> ) <sup>(a)</sup>		Rotational Constant B' (cm <sup>-1</sup> ) <sup>(b)</sup>	
h <sub>3</sub>	30,870	0.212	
d <sub>3</sub>	30,989	0.191	

Vibration	h <sub>3</sub> (a)	d <sub>3</sub> (a)	h <sub>3</sub> (b)	d <sub>3</sub> (b)	
e', 2 x 6	6	677(II)	664(II)	677	664
	--	--	1176	1145	
	8	1176(II)	1145(II)	1005	960
	19	--	--	1105	1048
a <sub>2</sub> <sup>''</sup>	4	359(I)	278(I)	359	278
	5	599(?)	559(I)	599	559
e <sup>''</sup>	10	508(I)	417(I)	508	417
	16	303(I)	273	308	280
a <sub>1</sub> <sup>'</sup>	12	1081	1035	1081	1035

a. Reference 8.

b. Reference 24.

TABLE 3. Summary of observed two-photon spectra of sym-triazine ( $h_3$ ) and ( $d_3$ ).

$\lambda_{vac}/\text{\AA}$ $h_3$	$2\sigma_{vac}/\text{cm}^{-1}$ $h_3$	$\Delta 2\sigma_{vac}/\text{cm}^{-1}$ $h_3$	$\Delta 2\sigma_{vac}/\text{cm}^{-1}$ $d_3$	I (a)	Assignments (b)
6634.0	30148	-729	-704	W } W }	$6_1^1 (A_1'')$
6630.9	30162	-715	-692		
6628.2	30174	-703	-680	W } W }	$6_1^0; 16_2^0$
6624.5	30191	-686	-664		
6578.7	30401	-576	-465	W	$6_1^1 (E'')$
6550.8	30531	-346	-313	W	$16_1^0 (c)$
6528.3	30636	-241		W	$6_1^0 16_0^1 (A_1'); 16_2^0 16_0^1 (A_1')$
6506.2	30740	-137	-115	W	$16_1^0 6_0^1 (E'') (c)$
6502.6	30757	-120		W	$6_1^2 (E''); 16_2^0 6_0^2 (E'')$
6482.4	30852	-24	-28	W	$6_0^1 (A_1'') (?); 16_1^1 (E')$
6480.7	30861	-16	-16	S } S } M }	Origin of $E''$ electronic state (30869)
6477.3	30877 (d)	0			
	30995		0		
6474.3	30891	14	10		
6459.0	30965	88	96	W } W } W }	$16_1^1 (A_1')$
6455.3	30982	105	111		
6454.2	30988	111			
6436.2	31074	198	185	M } S } M } M }	$6_0^1 (E'') (31096)$
6433.6	31087	210	201		
6432.6	31091	215	206		
6430.4	31102	225	218		

TABLE 3. (continued)

$\lambda_{\text{vac}}/\text{\AA}$ $h_3$	$2\sigma_{\text{vac}}/\text{cm}^{-1}$ $h_3$	$\Delta 2\sigma_{\text{vac}}/\text{cm}^{-1}$ $h_3$	$d_3$	I (a)	Assignments (b)
6414.3	31180	303	297 (e) 314 413	M	$16_1^1 6_0^1 (A_1')$
6387.1	31313	436	413	M	$16_0^1 (A_1') (c)$
6385.3	31322	445		M	$10_0^1 (A_1') (c) (?)$
6375.1	31372	495	476	W	$16_1^0 6_0^4 (E'')$ $\left[ 16_1^0 8_1^1 (E'') \text{ or } 16_1^0 19_0^1 (E'') \right] (c)$
6366.1	31416	539	535	S	
6362.8	31433	556	548	VS	
6360.0	31446	570	562	M	$6_0^2 (E'') (31425)$
6343.7	31527	650		$\left. \begin{matrix} W \\ W \end{matrix} \right\}$	$16_1^1 6_0^2 (A_1')$
6340.7	31542	665		$\left. \begin{matrix} M \\ M \\ M \end{matrix} \right\}$	
6338.2	31555	678	665	M	
6335.0	31570	693	675 (e) 680	M	$6_0^3 (E'') (31562)$
6332.1	31585	708	692	M	
6328.5	31603	726		W	
6309.0	31701	824	771	$\left. \begin{matrix} M \\ S \\ M \end{matrix} \right\}$	$6_0^4 (E'')$ $\left[ 8_0^1 (E'') \text{ or } 19_0^1 (E'') \right] (31705)$
6306.5	31713	836	791	S	
6303.0	31731	854	799 (e) 804	M	
6288.9	31802	925		W	
6270.4	31896	1019		W	
6267.1	31912	1036	996	VS	$12_0^1 6_0^1 (A_1')$
6263.1	31933	1056	1009	$\left. \begin{matrix} VS \\ VS \end{matrix} \right\}$	
6260.3	31948	1071	1020	VS	$12_0^1 (E'') (31940)$
6238.2	32061	1184		S	
6227.5	32116	1239		M	
6224.4	32131	1254		M	
6218.8	32160	1283	1224 (e) 1240	M	$12_0^1 6_0^1 (E'')$

TABLE 3. (Continued)

$\chi_{\text{vac}}/\text{Å}$ $h_3$	$2\sigma_{\text{vac}}/\text{cm}^{-1}$ $h_3$	$\Delta 2\sigma_{\text{vac}}/\text{cm}^{-1}$ $h_3$	$d_3$	I (a)	Assignments (b)
6207.8	32218	1340		S	
6203.9	32237	1360		S	
6199.3	32261	1385		S	
6175.8	32384	1507	1430	M	$12_0^1 16_0^1 (\Lambda_1')$
6156.5	32486	1609		S	
6153.3	32503	1626	1568	VS	
6149.8	32521	1644		S	$12_0^1 6_0^2 (E'')$
6148.1	32530	1653		S	
6141.4	32566	1689		M	
6128.8	32633	1756		S	
6120.7	32676	1799		VS	
6101.1	32781	1904		M	$12_0^1 6_0^4 (E'')$
6064.1	32981	2104		VS	$12_0^1 8_0^1 (E'')$ or $12_0^1 19_0^1 (E'')$
6055.0	33031	2154		M	
6051.5	33050	2173		M	
6034.6	33142	2265		M	
6030.3	33166	2289		M	

a. I = Intensity; W = Weak; M = Moderate; S = Strong; VS = Very Strong.

b. See text (Section IV) for explanations. Parenthetical symmetry is excited state symmetry. Rotationless origins are given in parentheses ( $\pm 3 \text{ cm}^{-1}$ ) for  $h_3$ -sym-triazine.

c. Feature shows change in intensity with circularly polarized light.

d. This strong, sharp feature is taken as the origin for purposes of measuring  $\Delta 2\sigma_{\text{vac}}$  and approximate vibrational intervals.

e. Features in  $d_3$  are split.

TABLE 4. Vibronic Symmetries and Selection Rules in an  $E''$  State.

$D_{3h}$ Vibrational Symmetry	Vibronic Symmetry of First Quantum in $E''$ Electronic State
$a'_1$	$E''$
$a'_2$	$E''$
$e'$	$A''_1, A''_2, E''$
$a''_2$	$E'$
$e''$	$A'_1, A'_2, E'$

Type	Vibronic Symmetry	Selection Rule
One-Photon	$A''_2$	$\Delta K = 0 \parallel$
	$E'$	$\Delta K = \pm 1 \perp$
Two-Photon	$A'_1$	$\Delta K = 0$ (a)
	$E''$	$\Delta K = \pm 1$
	$E'$	$\Delta K = \pm 2$

a. For  $A'_1 \leftarrow A'_1$  or  $E'' \leftarrow E''$  the transition symmetry is  $A'_1$  ( $\Delta K = 0$ ) and the isotropic part of the Q branch disappears if the transition is observed in circularly polarized light.

TABLE 5. Eigenvalue calculation for comparison purposes. (D is the LJT parameter, D' is the LPJT parameter, Q[a'] and Q[e'] are QJT parameters,  $\nu_6'$  is the unperturbed frequency, and  $\Delta E$  is the separation of  $1E''$  and  $1A_2''$ ).

20 Oscillators				
D = 0.8	D' = 0.0	Q[a'] = 0.1	Q[e'] = 0.1	$\nu_6' = 670 \text{ cm}^{-1}$
<u>E''</u>		<u>A''<sub>1</sub></u>	<u>A''<sub>2</sub></u>	
0.0		121.0730768	662.5011750	
544.2449932		836.4067343	1335.080923	
933.4890954		1594.795278	2030.169769	
1217.029648		1853.831997	2289.965194	
1452.966477		2370.623305	2781.397675	
1761.027421		2685.216268	3171.999172	
1880.895019		3036.137014	3306.544160	
2229.304175		3336.987600	3707.878153	
10 Oscillators				
D = 0.1	D' = 0.1	Q[a'] = 0.1	Q[e'] = 0.1	$\nu_6' = 670 \text{ cm}^{-1}$
		$\Delta E = 2000 \text{ cm}^{-1}$		
0.0		381.8399697	710.7872126	
709.6421346		1263.695364	1437.040730	
1006.593879		1719.539355	2038.781471	
1388.928001		2133.142081	2288.459417	
1613.615720		2480.052105	2317.805388	
1871.777141		3013.560704	2791.887116	
2115.287101		3137.603136	3080.915056	

TABLE 6. Calculated best fit for  $\nu_6$  energy levels in the  ${}^1E''$  state. (a)

$\nu_6' = 650 \text{ cm}^{-1}$ 
 $D = 0.05$ 
 $D' = 0.0$ 
 $Q[a'] = 0.0$ 
 $Q[e'] = 0.2$

$E''$			$A_1''$		$A_2''$		
Calc.	Obs.	n=0 coeff.	Calc.	Obs.	Calc.	Obs.	n=1 coeff.
0	0	.625	46	-24 (?)	665	677	.144
301	227	-.634	445	--	1060	1176	-.355
576	556	-.138	889	--	1369	--	.750
685	693	-.348					
917	836(?)	.055					

a. Frequencies in  $\text{cm}^{-1}$ ; rotationless spacings are given.



# APPENDIX

## Description of $(E'' + A_2'') \times e'$ Vibronic Coupling Calculation

A vibronic basis made up of electronic  $(\psi_{-1}^{E''}, \psi_{+1}^{E''}, \psi_{+1}^{A_2''})$  and two-dimensional harmonic oscillator functions  $(\chi_{N,L})$  is generated, and symmetry types  $E''$ ,  $A_1''$ , and  $A_2''$  are grouped together.  $E''$  basis functions of the  $(-1)$  type were used. For  $N = 0$  to  $N = 20$ ,  $L$  was run over its values  $N, N-2, \dots, 1$  or  $0$ . For a given  $(N,L)$ , basis functions were generated from the following forms.

	<u><math>E''</math></u>
$L = 0$	$\chi_{N,0} \psi_{-1}^{E''}$
$\text{MOD}(L,3)=0; \text{MOD}(L,2)=0;$ $L \neq 0$	$\sqrt{1/2} (\chi_{N,L} + \chi_{N,-L}) \psi_{-1}^{E''} (E'' \times a_1')$ AND $\sqrt{1/2} (\chi_{N,L} - \chi_{N,-L}) \psi_{-1}^{E''} (E'' \times a_2')$
$\text{MOD}(L,3)=0; \text{MOD}(L,2)=1$	$\sqrt{1/2} i (\chi_{N,L} - \chi_{N,-L}) \psi_{-1}^{E''} (E'' \times a_1')$ AND $\sqrt{1/2} i (\chi_{N,L} + \chi_{N,-L}) \psi_{-1}^{E''} (E'' \times a_2')$
$\text{MOD}(L,3)=1; \text{MOD}(L,2)=0$	$\chi_{N,L} \psi_{+1}^{E''}$ AND $\chi_{N,-L} \psi_{+1}^{A_2''}$
$\text{MOD}(L,3)=1; \text{MOD}(L,2)=1$	$-i \chi_{N,L} \psi_{+1}^{E''}$ AND $i \chi_{N,-L} \psi_{+1}^{A_2''}$
$\text{MOD}(L,3)=2; \text{MOD}(L,2)=0$	$\chi_{N,-L} \psi_{+1}^{E''}$ AND $\chi_{N,L} \psi_{+1}^{A_2''}$
$\text{MOD}(L,3)=2; \text{MOD}(L,2)=1$	$-i \chi_{N,-L} \psi_{+1}^{E''}$ AND $i \chi_{N,L} \psi_{+1}^{A_2''}$

$$\underline{A_1''}$$

$$\text{MOD}(L,3)=1; \text{MOD}(L,2)=0$$

$$\sqrt{1/2} (\chi_{N,L} \psi_{-1}^{E''} + \chi_{N,-L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=1; \text{MOD}(L,2)=1$$

$$\sqrt{1/2} i (-\chi_{N,L} \psi_{-1}^{E''} + \chi_{N,-L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=2; \text{MOD}(L,2)=0$$

$$\sqrt{1/2} (\chi_{N,-L} \psi_{-1}^{E''} + \chi_{N,L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=2; \text{MOD}(L,2)=1$$

$$\sqrt{1/2} i (-\chi_{N,-L} \psi_{-1}^{E''} + \chi_{N,L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=0; \text{MOD}(L,2)=0;$$

$$L \neq 0$$

$$\sqrt{1/2} (\chi_{N,L} - \chi_{N,-L}) \psi^{A_2''}$$

$$\text{MOD}(L,3)=0; \text{MOD}(L,2)=1$$

$$\sqrt{1/2} i (\chi_{N,L} + \chi_{N,-L}) \psi^{A_2''}$$

$$\underline{A_2''}$$

$$\text{MOD}(L,3)=1; \text{MOD}(L,2)=0$$

$$\sqrt{1/2} (\chi_{N,L} \psi_{-1}^{E''} - \chi_{N,-L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=1; \text{MOD}(L,2)=1$$

$$-\sqrt{1/2} i (\chi_{N,L} \psi_{-1}^{E''} + \chi_{N,-L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=2; \text{MOD}(L,2)=0$$

$$\sqrt{1/2} (\chi_{N,-L} \psi_{-1}^{E''} - \chi_{N,L} \psi_{+1}^{E''})$$

$$\text{MOD}(L,3)=2; \text{MOD}(L,2)=1$$

$$-\sqrt{1/2} i (\chi_{N,-L} \psi_{-1}^{E''} + \chi_{N,L} \psi_{+1}^{E''})$$

$$L=0$$

$$\chi_{N,0} \psi^{A_2''}$$

$$\text{MOD}(L,3)=0; \text{MOD}(L,2)=0; L \neq 0$$

$$\sqrt{1/2} (\chi_{N,L} + \chi_{N,-L}) \psi^{A_2''}$$

$$\text{MOD}(L,3)=0; \text{MOD}(L,2)=1$$

$$\sqrt{1/2} i (\chi_{N,L} - \chi_{N,-L}) \psi^{A_2''}$$

The basis functions can be written in the general form

$$\begin{aligned} \Phi_{N,L} = & (a \chi_{N,L} + b \chi_{N,-L}) \psi_{-1}^{E''} + (c \chi_{N,L} + d \chi_{N,-L}) \psi_{+1}^{E''} \\ & + (e \chi_{N,L} + f \chi_{N,-L}) \psi^{A_2''} \end{aligned}$$

Once the basis is generated, the matrix elements must be calculated. Only the upper (or lower) half of the matrix need be calculated, since the matrix is symmetric.

For linear JT coupling within the E" state we need the matrix Hamiltonian

$$\mathcal{H}_{LJT} = \begin{bmatrix} \mathcal{H}_0 & ikQ_- & 0 \\ -ikQ_+ & \mathcal{H}_0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

and the primitive matrix elements

$$\langle \chi_{N,L} | Q_{\pm} | \chi_{N+1, L \mp 1} \rangle = ((N \mp L + 2)/2\alpha)^{1/2} \quad \alpha = \omega/\hbar$$

The LJT matrix elements can be worked out to

$$\langle \phi_{N,L} | \mathcal{H}_{LJT} | \phi_{N+1, L+1} \rangle = i\hbar\omega ((N+L+2)D)^{1/2} (a^*c' - d^*b')$$

$$\langle \phi_{N,L} | \mathcal{H}_{LJT} | \phi_{N+1, L-1} \rangle = i\hbar\omega ((N-L+2)D)^{1/2} (b^*d' - c^*a')$$

in which the primed coefficients are from the ket basis function, and  $D = \frac{k^2}{2\hbar\omega^3}$

Similarly, the quadratic Hamiltonians are

$$\mathcal{H}_{QJT}^{a'} = \begin{bmatrix} \mathcal{H}_0 + \frac{Ca}{2} Q_+ Q_- & 0 & 0 \\ 0 & \mathcal{H}_0 + \frac{Ca}{2} Q_+ Q_- & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathcal{H}_{QJT}^{e'} = \begin{bmatrix} \mathcal{H}_0 & C_e Q_+^2 & 0 \\ C_e Q_-^2 & \mathcal{H}_0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The relevant primitive matrix elements are

$$\langle N, L | Q_{\pm}^2 | N, L \pm 2 \rangle = \frac{1}{2\alpha} (4(N \mp L)(N \pm L + 2))^{1/2}$$

$$\langle N, L | Q_{\pm}^2 | N+2, L \pm 2 \rangle = \frac{1}{2\alpha} ((N \pm L + 2)(N \pm L + 4))^{1/2}$$

$$\langle N, L | Q_+ Q_- | N, L \rangle = \frac{1}{2\alpha} (2N+2)$$

$$\langle N, L | Q_+ Q_- | N+2, L \rangle = \frac{1}{2\alpha} ((N+L+2)(N-L+2))^{1/2}$$

The quadratic JT diagonal matrix elements are then  $\langle E'' \times a_1'' | \mathcal{H}_{QJT}^{a'} | E'' \times a_2'' \rangle = 0$

$$\langle \phi_{N,L} | \mathcal{H}_{QJT}^{a'} | \phi_{N,L} \rangle = \hbar\omega (1 + Q[a']/2)(N+1) \quad Q[a'] = \frac{C_a}{\omega^2}$$

$$\langle \phi_{N,1} | \mathcal{H}_{QJT}^{e'} | \phi_{N,1} \rangle = 2Q[e'] \hbar\omega (N+1)(a^* d' + d^* a') \quad Q[e'] = \frac{C_e}{2\omega^2}$$

For diagonal in N, off diagonal in L we have

$$\langle \phi_{N,L} | \mathcal{H}_{QJT}^{e'} | \phi_{N,L+2} \rangle = 2Q[e'] \hbar\omega ((N-L)(N+L+2))^{1/2} (b^* d' + c^* a')$$

$$\langle \phi_{N,L} | \mathcal{H}_{QJT}^{e'} | \phi_{N,L-2} \rangle = 2Q[e'] \hbar\omega ((N+L)(N-L+2))^{1/2} (a^* c' + d^* b')$$

These two formulas must be corrected for  $L = 0$  in either the bra or ket, since they do not account for the fact that since  $L = -L$ , a primitive matrix element that is usually zero is non-zero. For  $\langle \phi_{N,0} | \mathcal{H}_{QJT}^{e'} | \phi_{N,2} \rangle$ ,  $2Q[e'] \hbar\omega (N(N+2))^{1/2} d'$  must be added to the above and for  $\langle \phi_{N,2} | \mathcal{H}_{QJT}^{e'} | \phi_{N,0} \rangle$ ,  $2Q[e'] \hbar\omega (N(N+2))^{1/2} d^*$  must be added to the above. The quadratic matrix elements off diagonal in N and diagonal in L are

$$\langle \phi_{N,L} | \mathcal{H}_{QJT}^{a'} | \phi_{N+2,L} \rangle = \frac{\hbar\omega}{4} Q[a] ((N+L+2)(N-L+2))^{1/2} (a^* a' + b^* b' + c^* c' + d^* d')$$

$$\langle \phi_{N,1} | \mathcal{H}_{QJT}^{e'} | \phi_{N+2,1} \rangle = \hbar\omega Q[e] ((N+1)(N+3))^{1/2} (a^* d' + d^* a')$$

The quadratic matrix elements off diagonal in N and L are

$$\langle \phi_{N,L} | \mathcal{H}_{QJT}^{e'} | \phi_{N+2,L+2} \rangle = \hbar\omega Q[e] ((N+L+2)(N+L+4))^{1/2} (b^* d' + c^* a')$$

$$\langle \phi_{N,L} | \mathcal{H}_{QJT}^{e'} | \phi_{N+2,L-2} \rangle = \hbar\omega Q[e] ((N-L+2)(N-L+4))^{1/2} (a^* c' + d^* b')$$

Again for L = 0 in the bra or ket we must correct the formulas. For  $\langle \phi_{N,0} | \mathcal{H}_{QJT}^{e'} | \phi_{N+2,2} \rangle$

add  $\hbar\omega Q[e] ((N+2)(N+4))^{1/2} d'$ , and for  $\langle \phi_{N,2} | \mathcal{H}_{QJT}^{e'} | \phi_{N+2,0} \rangle$

add  $\hbar\omega Q[e] ((N+2)N)^{1/2} d^*$ .

The matrix elements up to n = 10 were also hand calculated, and the hand calculation checked by the upper half of the matrix agreeing with the lower half.

The pseudo-Jahn Teller interaction between the E" and A<sub>2</sub>" was completed for basis functions to N = 10, and the matrix elements were hand calculated. The PJT matrix Hamiltonian is

$$\mathcal{H}_{PJT} = \begin{bmatrix} 0 & 0 & -ik'Q_+ \\ 0 & 0 & -ik'Q_- \\ ik'Q_- & ik'Q_+ & 0 \end{bmatrix}$$

We have derived the PJT matrix element formulas. They are as follows, with

$$D' = \frac{(k')^2}{2\hbar\omega^3} :$$

$$\langle \phi_{N,L} | \mathcal{H}_{PJT} | \phi_{N+1,L+1} \rangle = -i\hbar\omega ((N+L+2)D')^{1/2} (b^*f' + c^*e')$$

$$\langle \phi_{N,L} | \mathcal{H}_{PJT} | \phi_{N+1,L-1} \rangle = -i\hbar\omega ((N-L+2)D')^{1/2} (a^*e' + d^*f')$$

$$\langle \phi_{N,L} | \mathcal{H}_{PJT} | \phi_{N-1,L+1} \rangle = -i\hbar\omega ((N-L)D')^{1/2} (b^*f' + c^*e')$$

$$\langle \phi_{N,L} | \mathcal{H}_{PJT} | \phi_{N-1,L-1} \rangle = -i\hbar\omega ((N+L)D')^{1/2} (a^*e' + d^*f')$$

We have the following additional factors:

$$\text{for } \langle \phi_{N,0} | \mathcal{H}_{PJT} | \phi_{N+1,1} \rangle \quad \text{add } -i\hbar\omega ((N+2)D')^{1/2} f'$$

$$\text{for } \langle \phi_{N,1} | \mathcal{H}_{PJT} | \phi_{N+1,0} \rangle \quad \text{add } -i\hbar\omega ((N+1)D')^{1/2} d^*$$

$$\text{for } \langle \phi_{N,0} | \mathcal{H}_{PJT} | \phi_{N-1,1} \rangle \quad \text{add } -i\hbar\omega (ND')^{1/2} f'$$

$$\text{for } \langle \phi_{N,1} | \mathcal{H}_{PJT} | \phi_{N-1,0} \rangle \quad \text{add } -i\hbar\omega ((N+1)D')^{1/2} d^*$$

FIGURE CAPTIONS

- 1a. Ground state  $n, \pi$  electronic structure.
- 1b.  $\pi^* \leftarrow n$  spectroscopic transitions.
2. Role of vibronic coupling in single vibronic level fluorescence (SVLF). See text (Section II) for detailed discussion. The left hand side of the figure shows the electronic symmetry and the numbers indicate the number of quanta of  $\nu_6$ . The right hand side shows the relevant vibronic symmetries of the levels. Double-ended arrows show vibronic coupling pathways. Single-ended arrows going down indicate possible emission. Solid lines are the LJT coupling case, dashed lines are the QJT coupling case.
3. Experimental two photon photoacoustic apparatus (see text for discussion).
4. Survey two photon photoacoustic spectrum of  $h_3$ -sym-triazine. Arrows indicate rotationless origins of labeled features. Horizontal axis is not linear in frequency, but in wavelength.
- 5a. Experimental rotational contour for  $d_3$ -sym-triazine  ${}^1E''$  origin. Rotationless origin is marked with an arrow. Shoulder at low energy side of contour could be related to presence of  $6_0^1 (A'')$ . See text, Section IV for discussion.
- 5b. Calculated rotational contour of origin with  $\Delta K = \pm 1$ ,  $B'' = .19358 \text{ cm}^{-1}$ ,  $B' = .1916 \text{ cm}^{-1}$ ,  $C'' = B''/2$ ,  $C' = B'/2$ ,  $\zeta = +0.1$ ,  $T = 298 \text{ K}$ . Frequency scale is same as for Figure 5a. Note missing shoulder on low energy side of contour.
- 6a. Experimental rotational contour for  $d_3$ -sym-triazine  $6_0^2$ . Rotationless origin is marked with an arrow.



- 6b. Calculated rotational contour of  $6_0^2$  with  $\Delta K = \pm 1$ ,  $B'' = .19358 \text{ cm}^{-1}$ ,  $B' = .1916 \text{ cm}^{-1}$ ,  $C'' = B''/2$ ,  $C' = B'/2$ ,  $\zeta = +0.1$ ,  $T = 298 \text{ K}$ .  
Frequency scale is same as for Figure 6a.
- 7a. Experimental rotational contour for  $d_3$ -sym-triazine  $6_0^3$ . Rotationless origin is marked with an arrow.
- 7b. Calculated rotational contour of  $6_0^3$  with  $\Delta K = \pm 1$ ,  $B'' = .19358 \text{ cm}^{-1}$ ,  $B' = .1915 \text{ cm}^{-1}$ ,  $C'' = B''/2$ ,  $C' = B'/2$ ,  $\zeta = 0.0$ ,  $T = 298 \text{ K}$ . Frequency scale is same as Figure 7a.
- 8a. Experimental rotational contour for  $d_3$ -sym-triazine  $6_0^1$ . Rotationless origin is marked with an arrow.
- 8b. Calculated rotational contour of  $6_0^1$  with  $\Delta K = \pm 1$ ,  $B'' = .19358 \text{ cm}^{-1}$ ,  $B' = .1962 \text{ cm}^{-1}$ ,  $C'' = B''/2$ ,  $C' = B'/2$ ,  $\zeta = -0.1$ ,  $T = 298 \text{ K}$ .  
Frequency scale is same as for Figure 8a.
- 8c. Experimental rotational contour for  $h_3$ -sym-triazine  $6_0^1$ . Rotationless origin is marked with an arrow.
- 8d. Calculated rotational contour with  $\Delta K = \pm 1$ ,  $B'' = .2146 \text{ cm}^{-1}$ ,  $B' = .2172 \text{ cm}^{-1}$ ,  $C'' = B''/2$ ,  $C' = B'/2$ ,  $\zeta = 0.0$ ,  $T = 298 \text{ K}$ . Frequency scale is same as for Figure 8c.
9. Experimental rotational contour for  $h_3$ -sym-triazine  $16_0^1 (A_1')$  in both linear and circular polarization. Rotationless origin is marked with an arrow. The second polarized peak is a different transition, probably  $10_0^1 (A_1')$ .
10. Effect of LPJT parameter  $D'$  on first quantum of  $e'$  vibration in  ${}^1E''$  electronic state.  $\nu_6' = 670 \text{ cm}^{-1}$ .  $D$ ,  $Q[a']$ ,  $Q[e']$  are zero,  $\Delta E$ , the separation of the  $E''$  and  $A_2''$  electronic states is  $1500 \text{ cm}^{-1}$ . Note that for this case, as well as for the LJT parameter  $D$ , the  $A_2''$  level is below the  $E''$  level, contrary to observation.

11. Effect of QJT parameter  $Q[e']$  on  $\nu_6$  energy levels in  ${}^1E''$  state with small LJT parameter  $D = 0.05$ , and  $D' = 0.0$ ,  $Q[a'] = 0.0$ ,  $\nu_6' = 670 \text{ cm}^{-1}$ . Best fit (see Table VI) was found with  $Q[e'] = 0.2$ , but with  $\nu_6' = 650 \text{ cm}^{-1}$ .

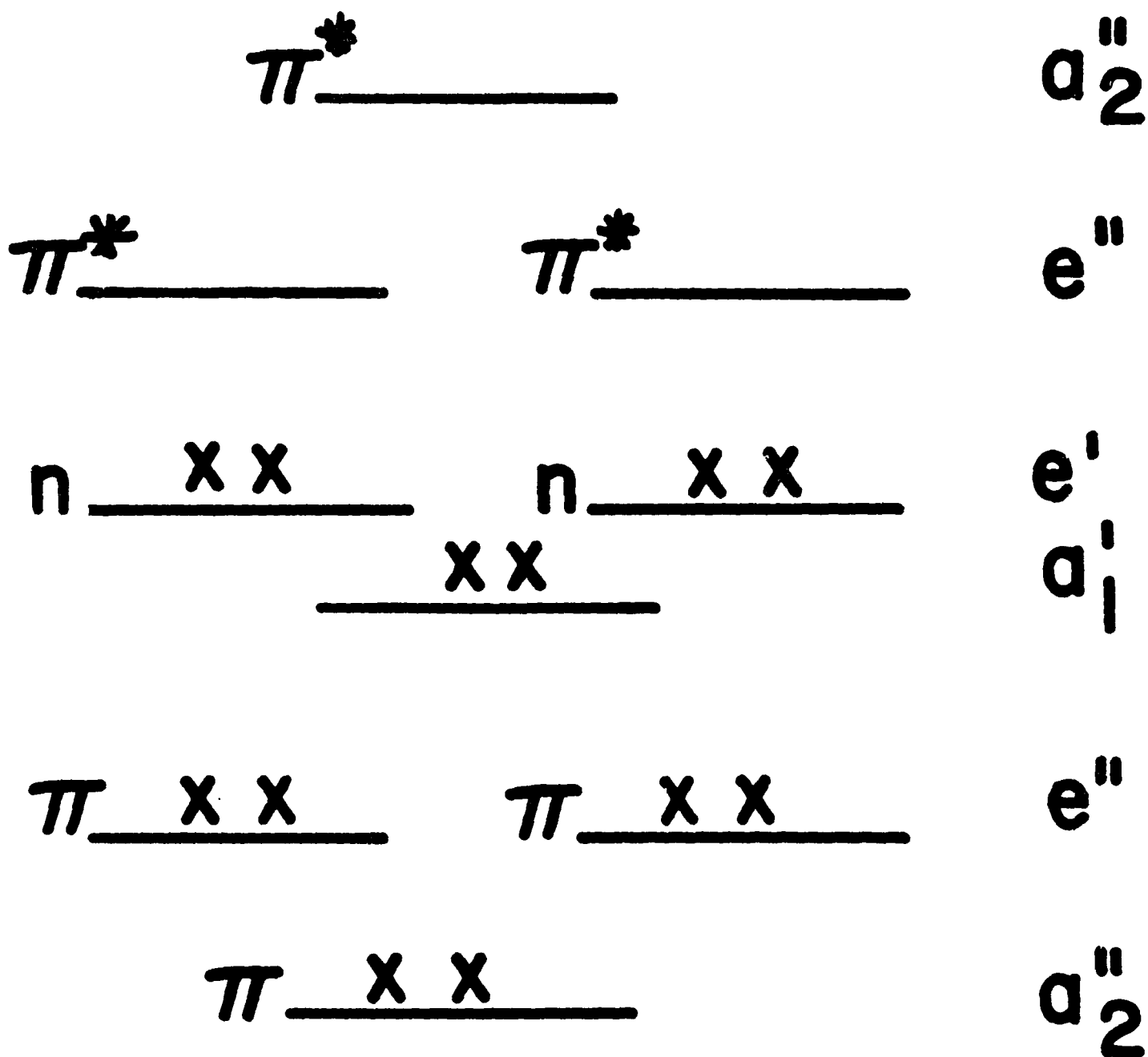


FIGURE 1a

ELECTRON PROMOTION	STATE SYMMETRY	TRANSITION TYPE
$\pi^*(e'') \leftarrow n(e')$	$E''$	2 PHOTON
	$A_2''$	1 PHOTON
	$A_1''$	<hr/>
$\pi^*(e'') \leftarrow n(a_1')$	$E''$	2 PHOTON

FIGURE 1b

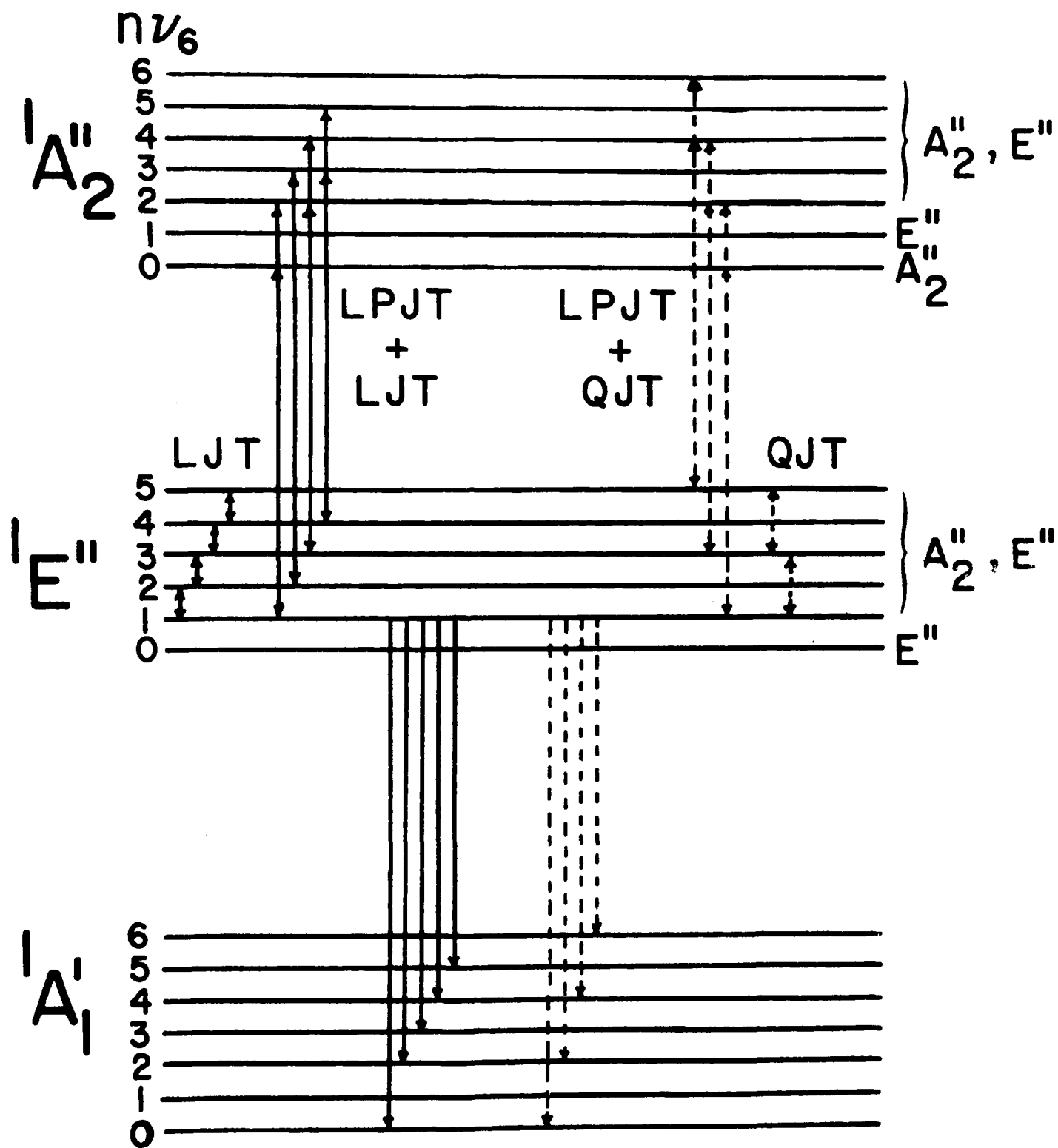


FIGURE 2

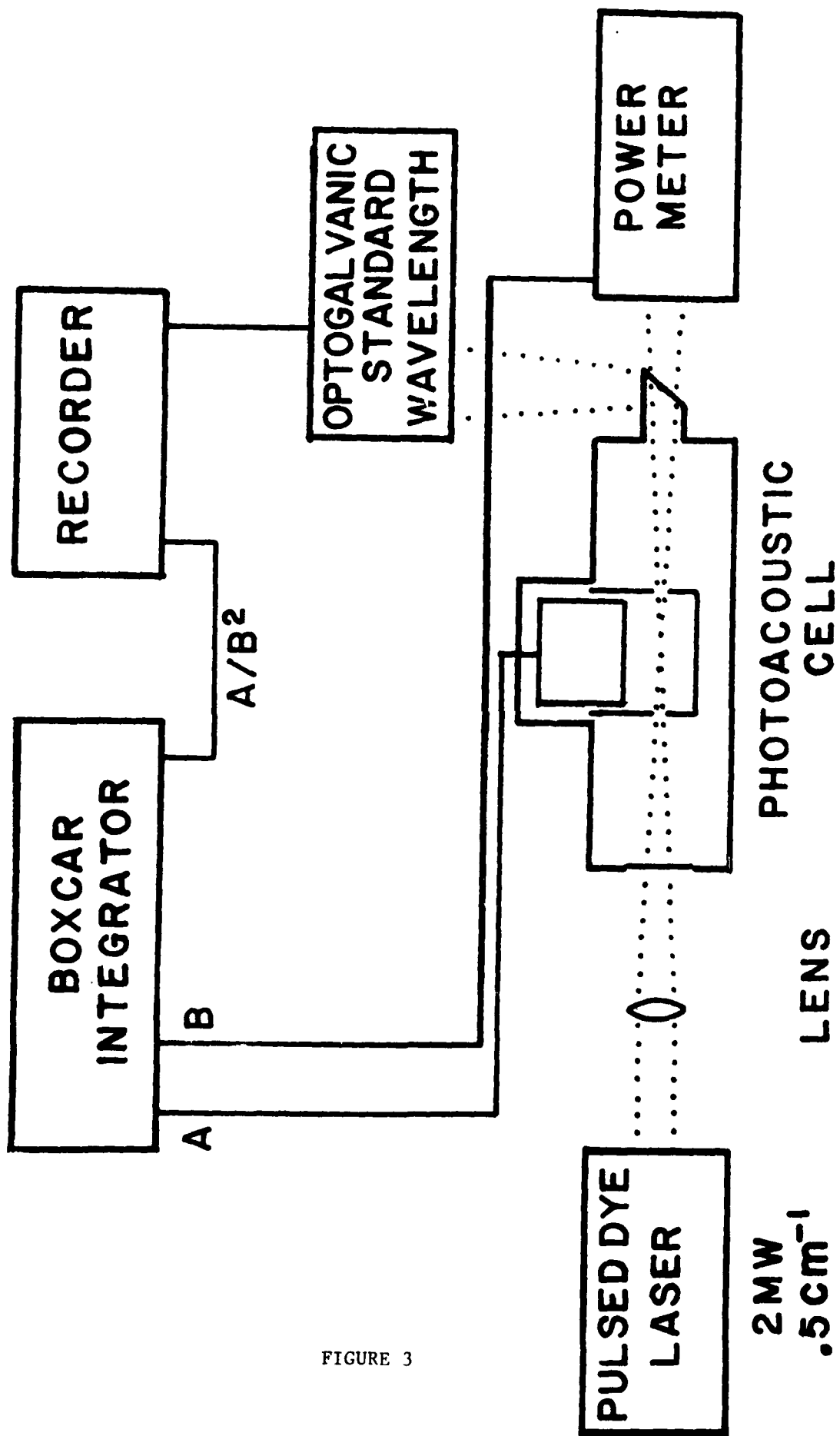


FIGURE 3

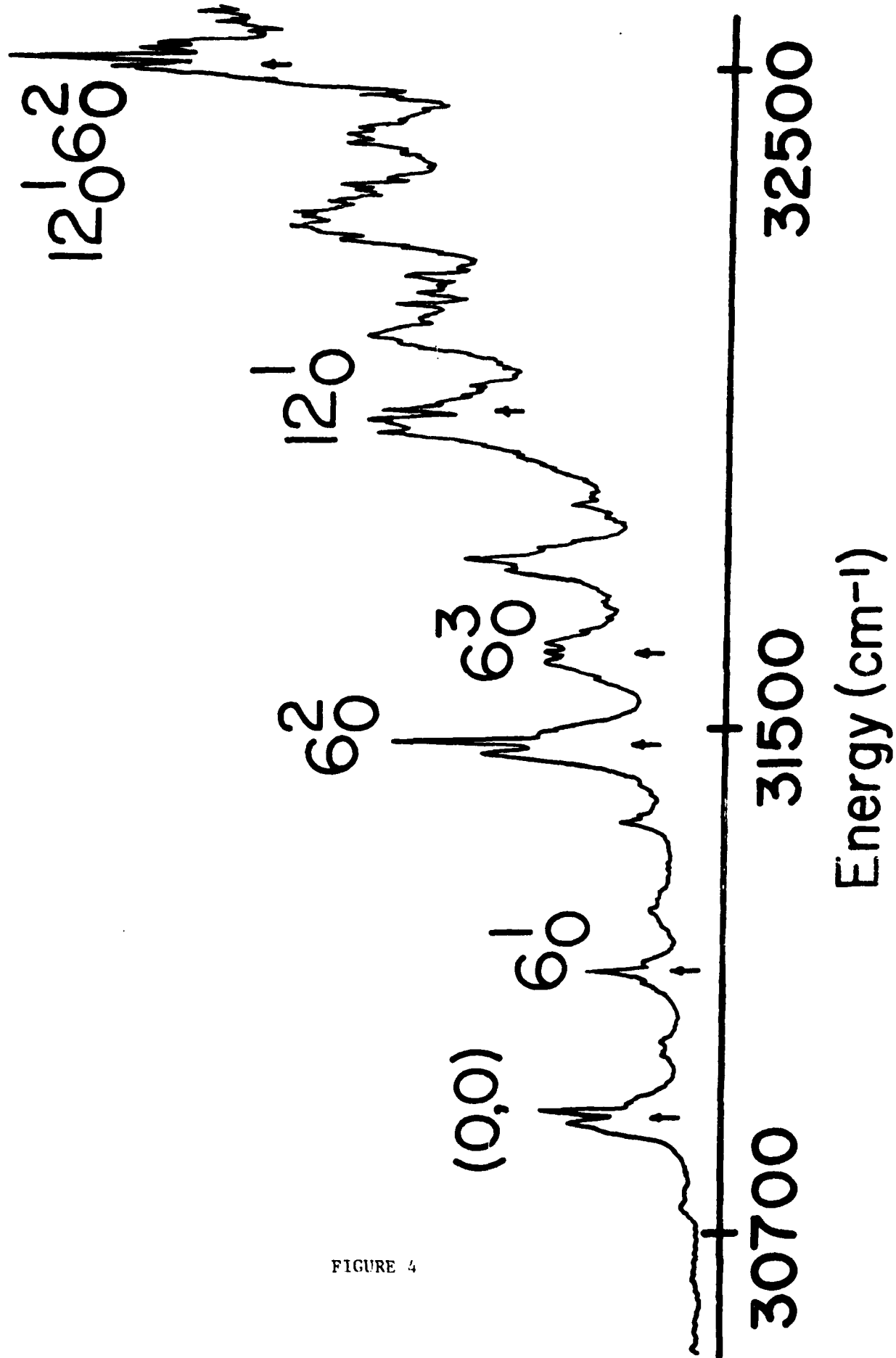


FIGURE 4

$d_3$ -Origin

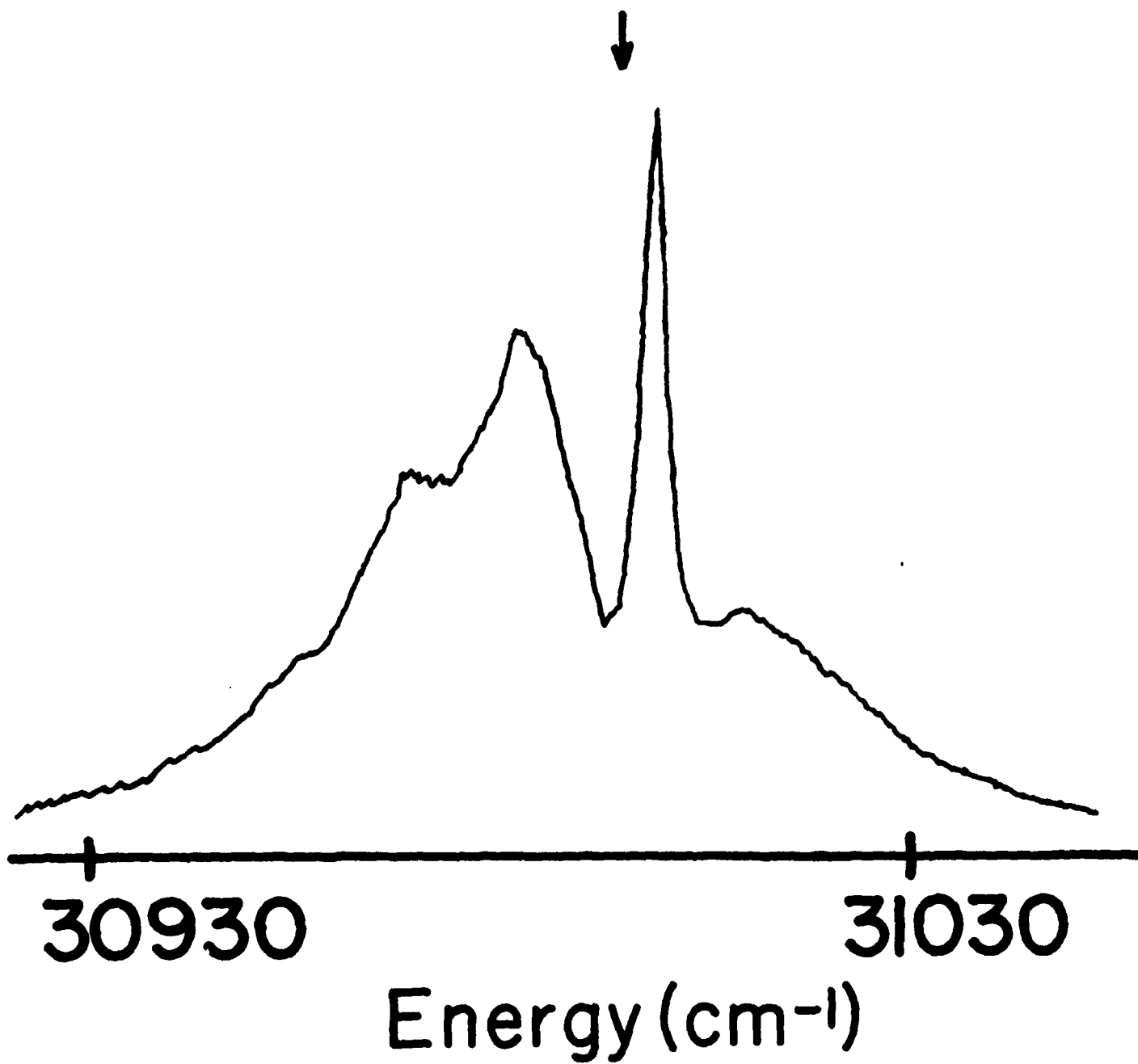


FIGURE 5a



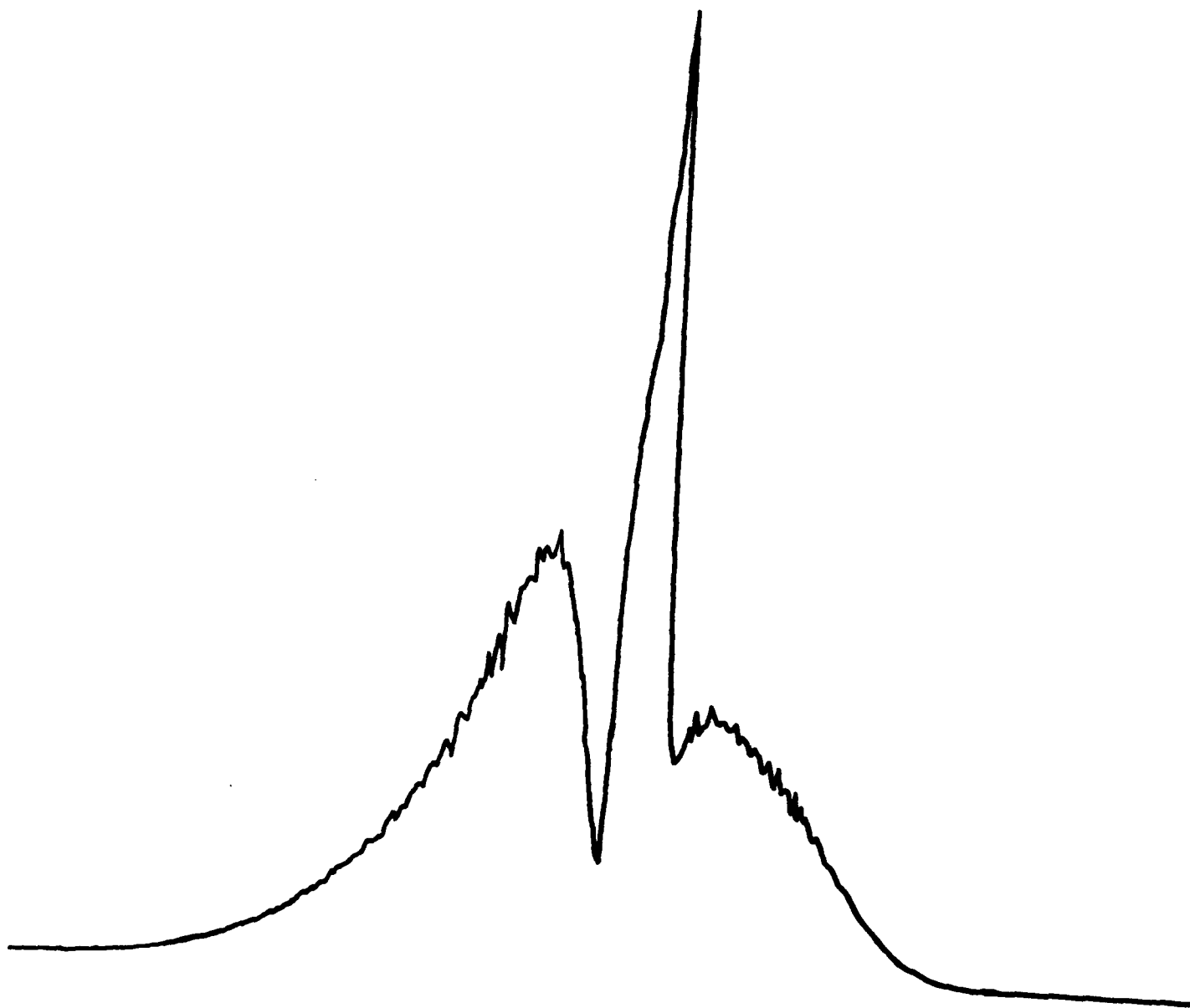


FIGURE 5b

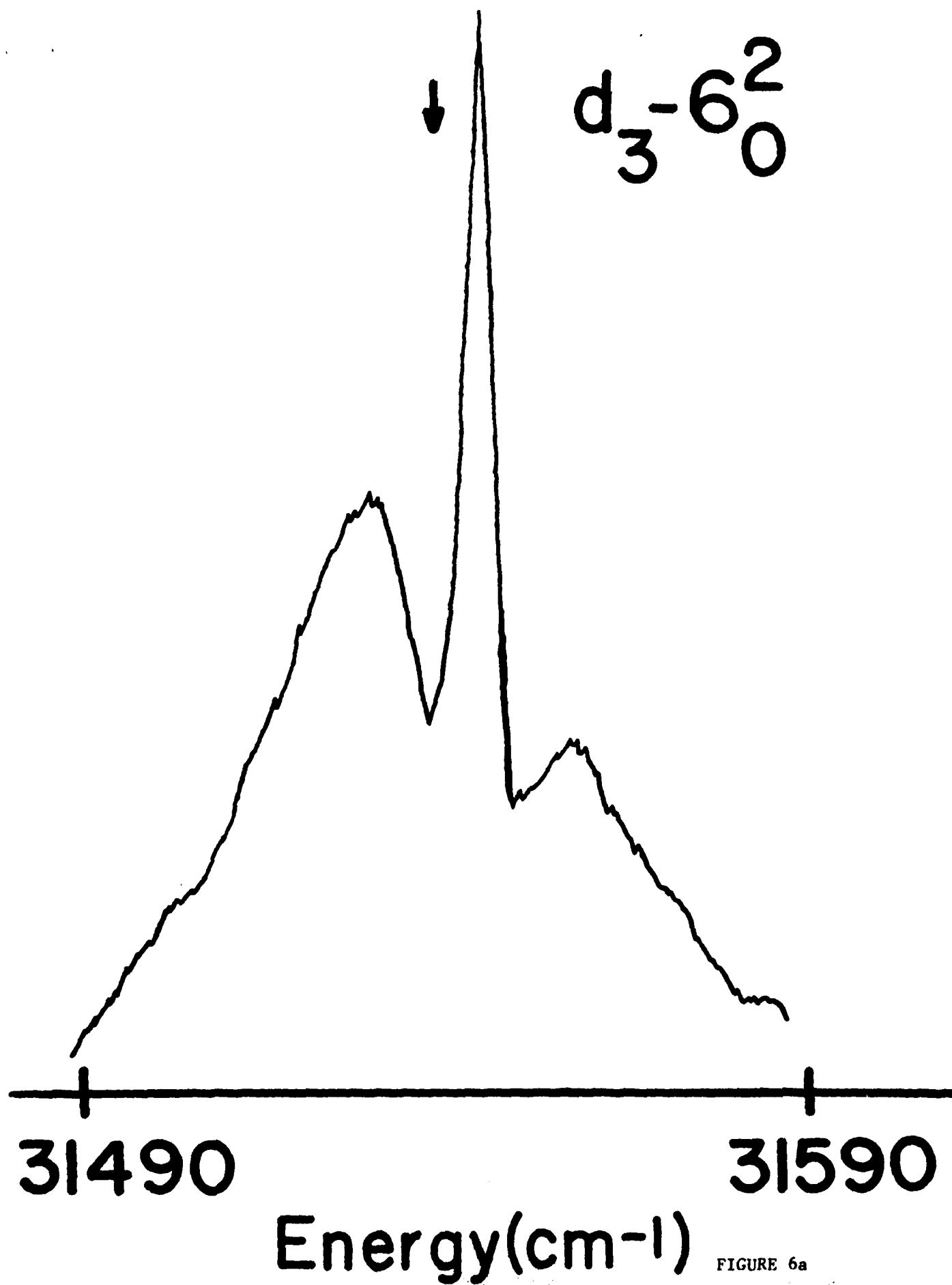


FIGURE 6a

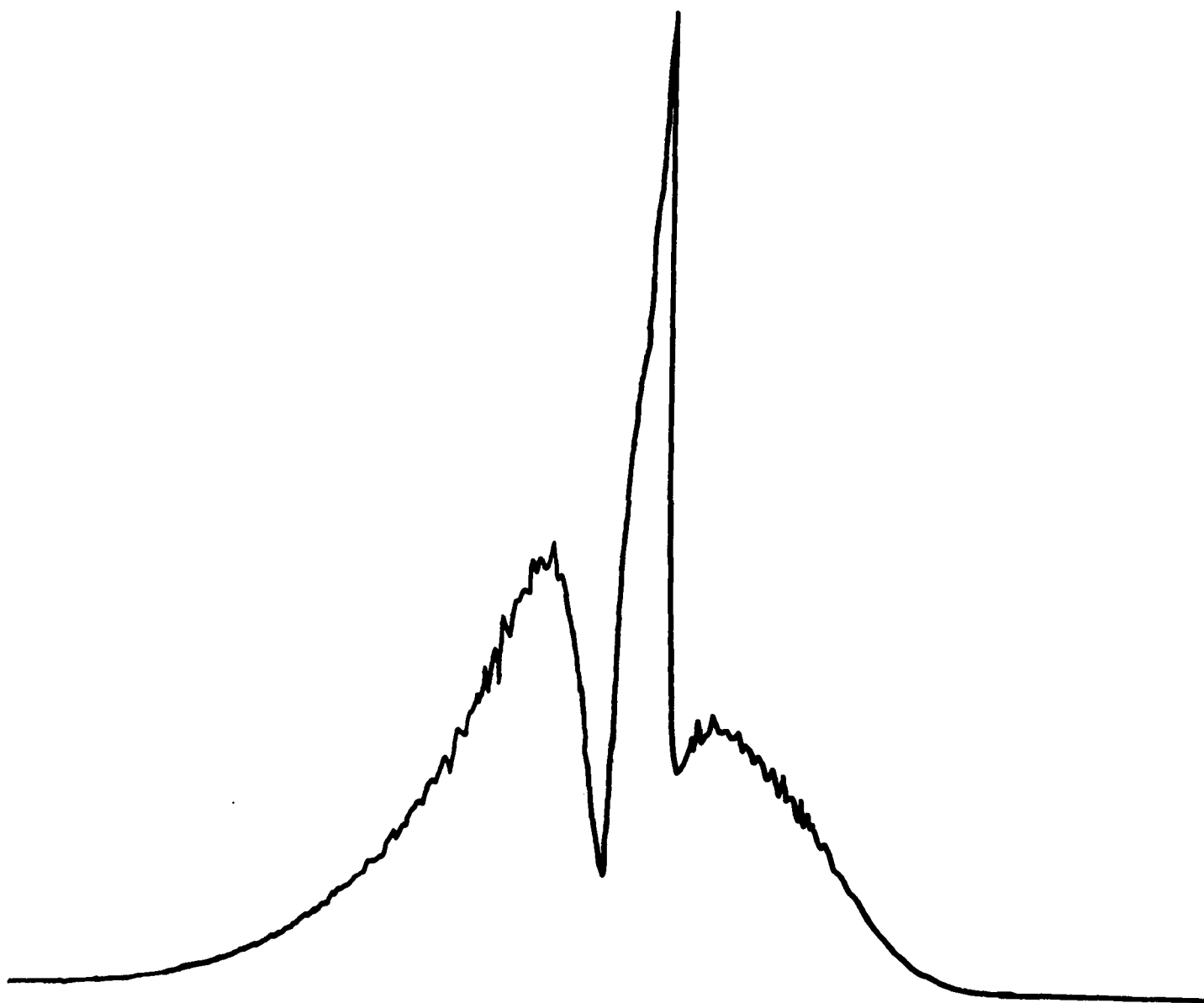


FIGURE 6b

$d_3-6_0^3$

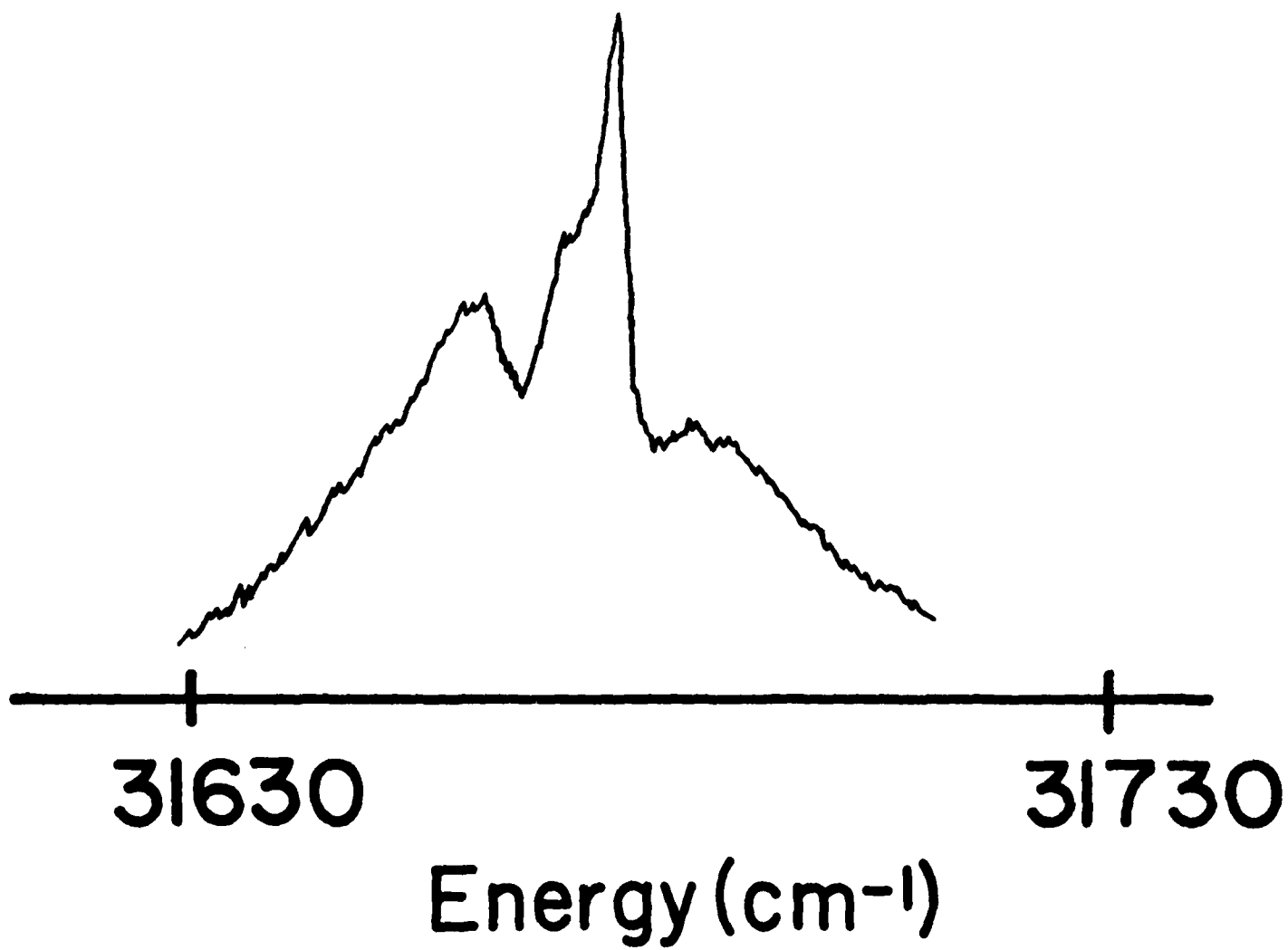


FIGURE 7a

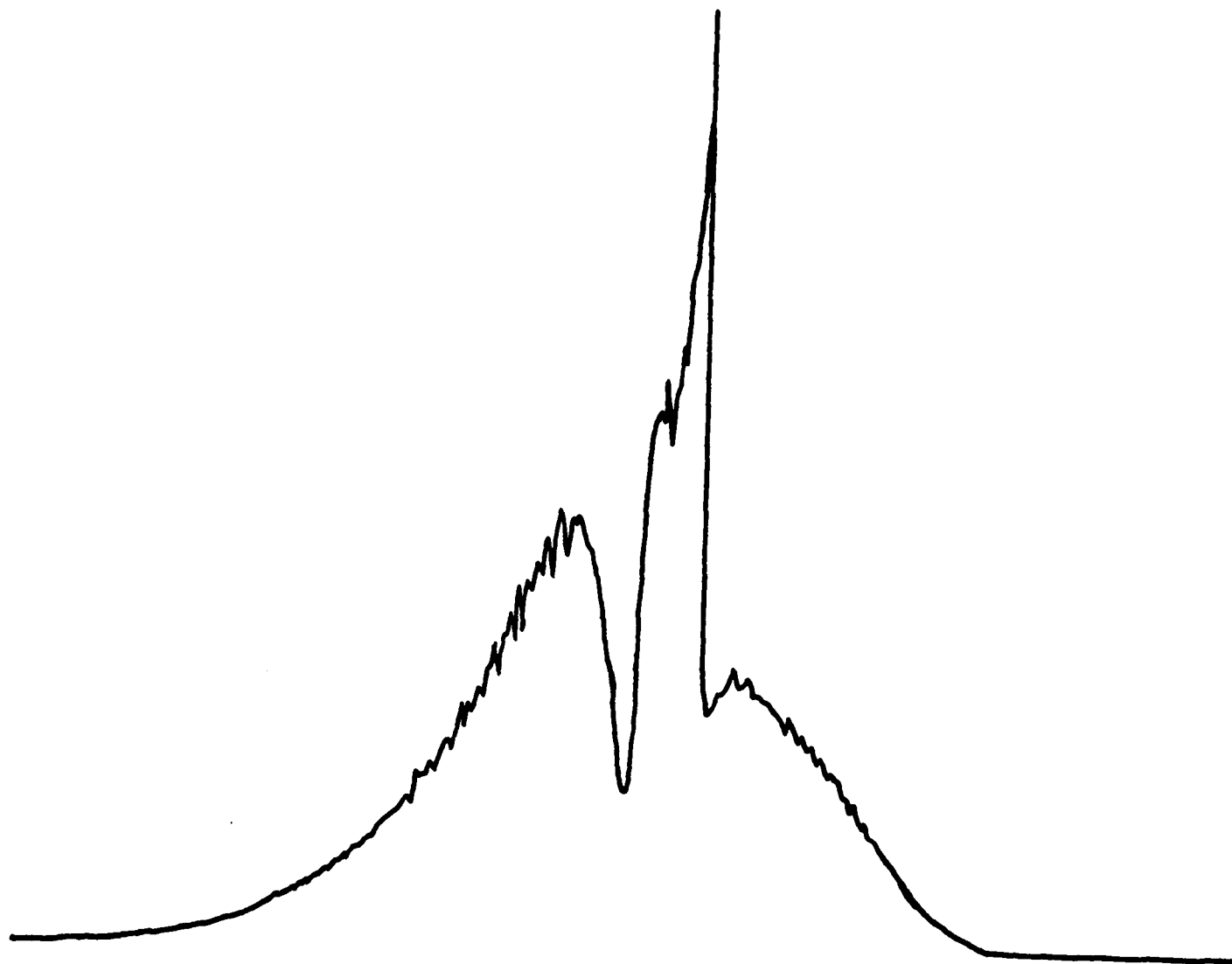


FIGURE 7b

$d_3-6_0^1$

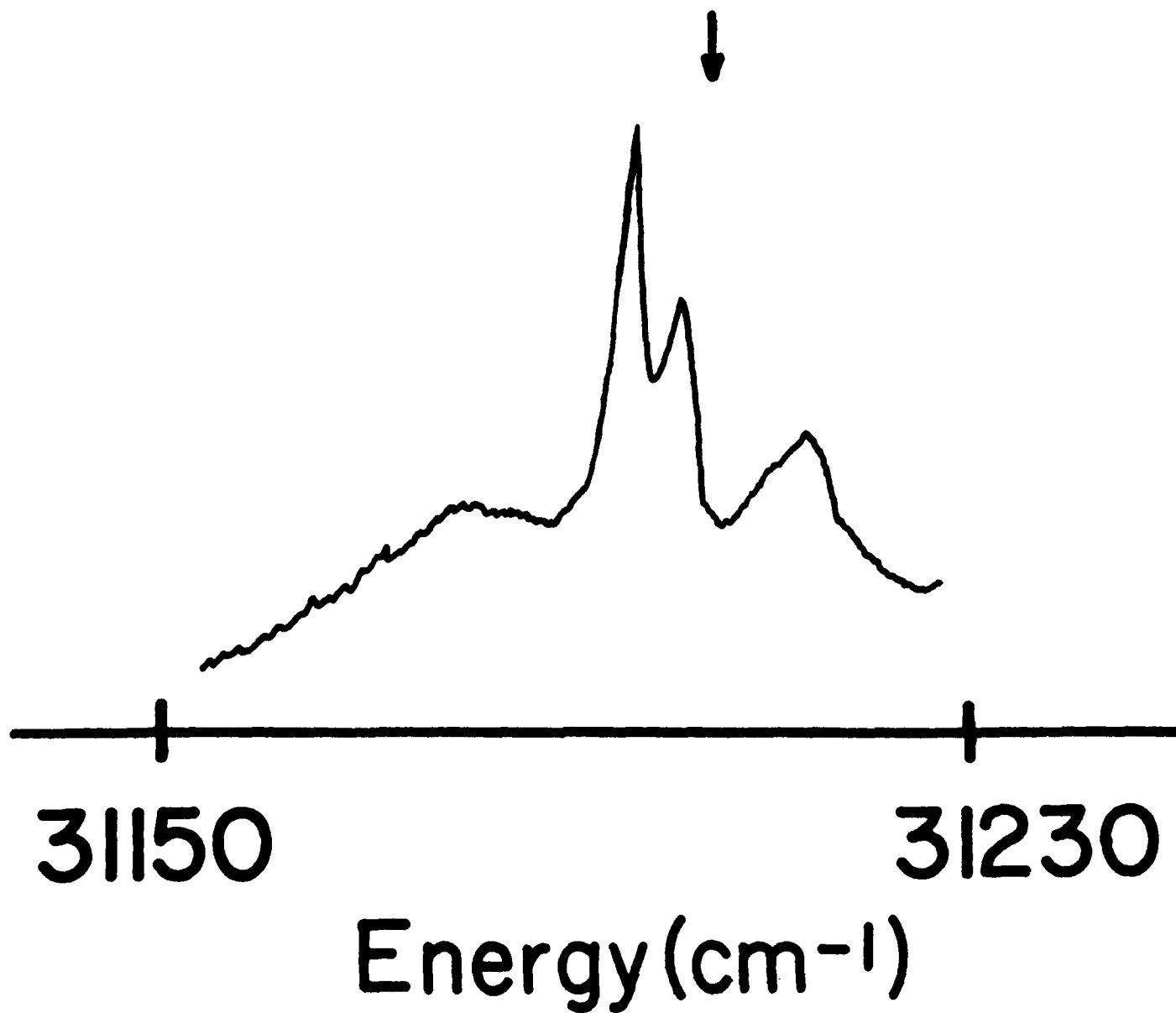


FIGURE 8a

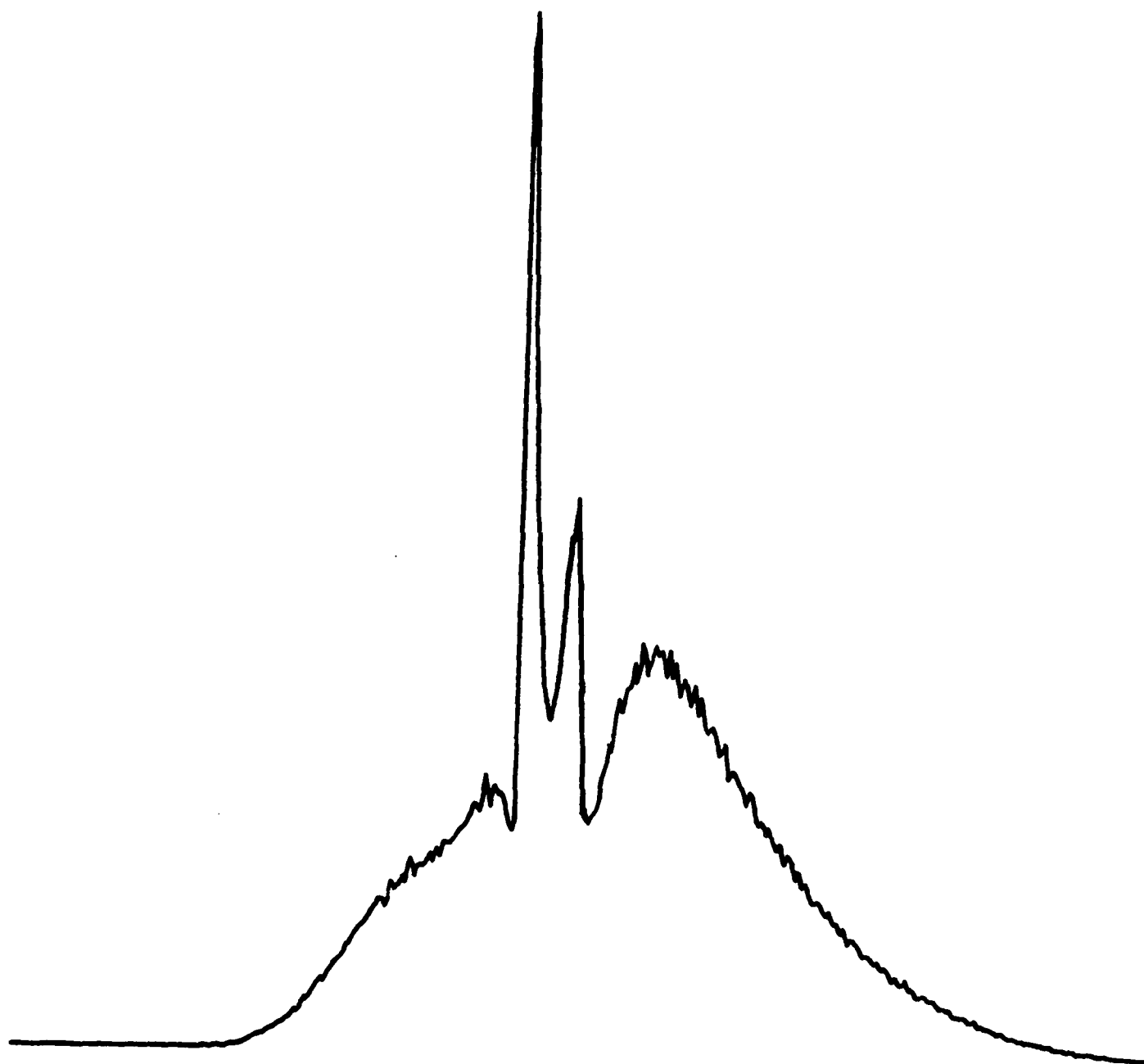


FIGURE 8b

$h_3-6^1_0$

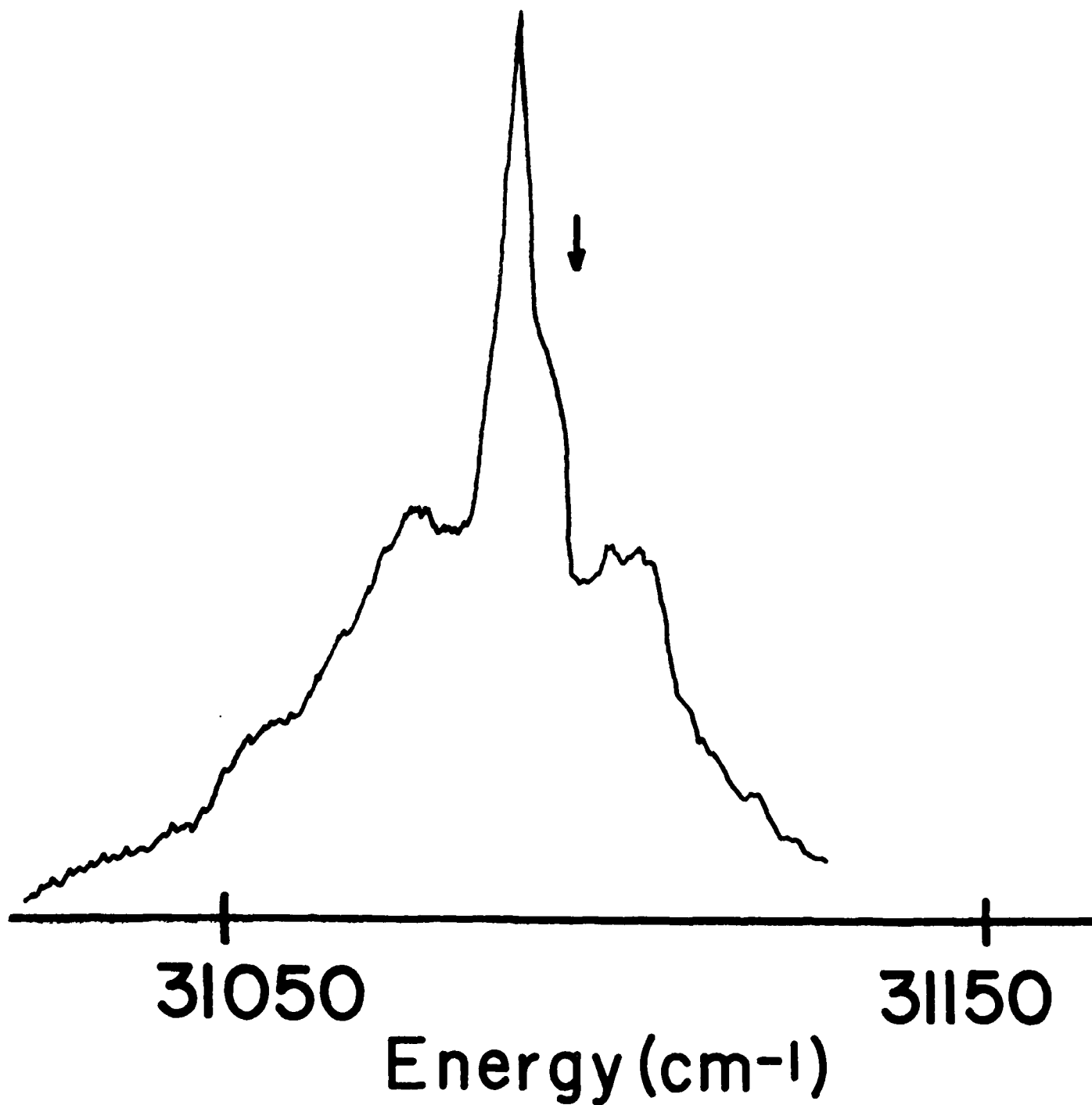


FIGURE 8c



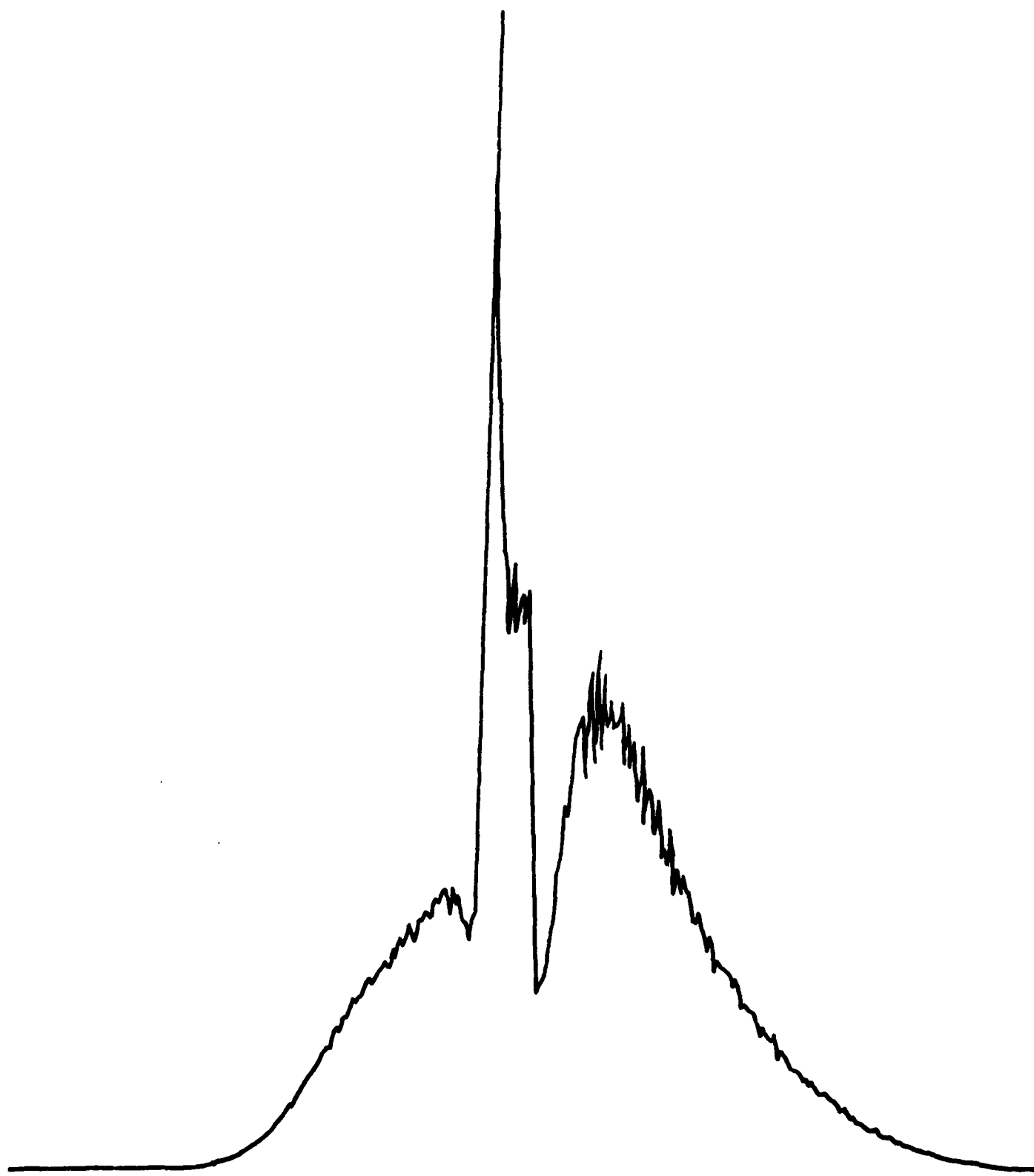


FIGURE 8d

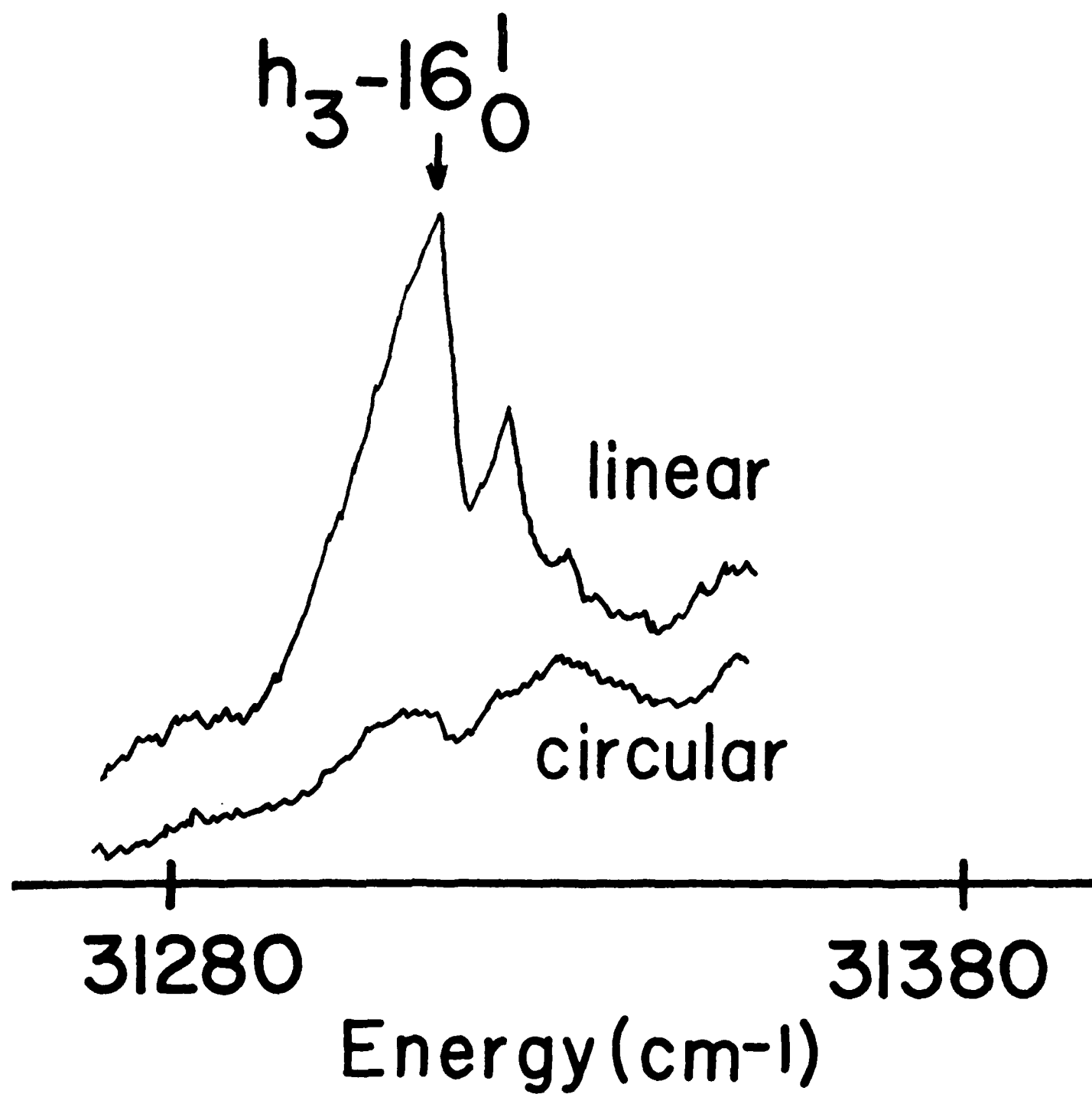


FIGURE 9

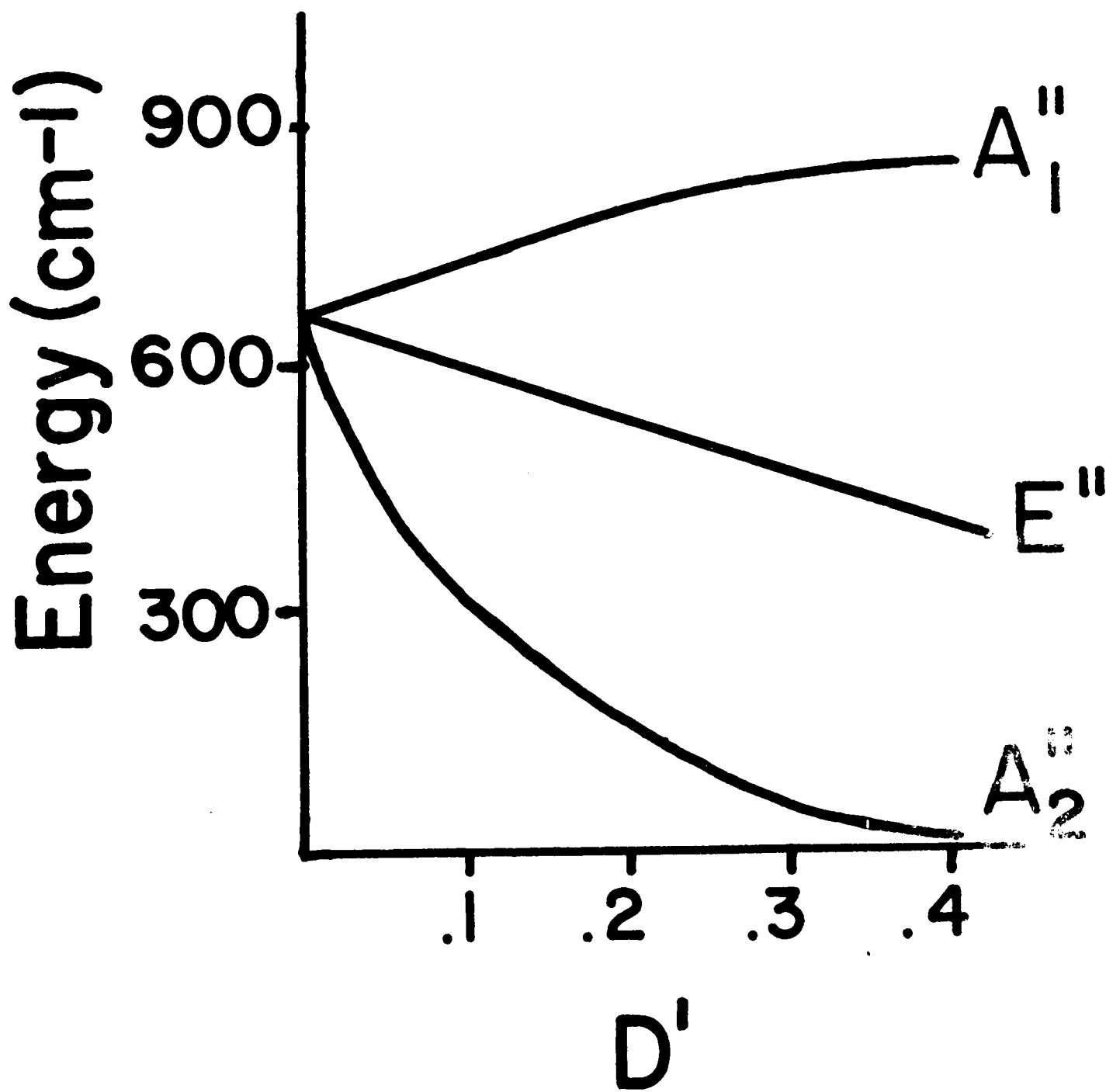


FIGURE 10

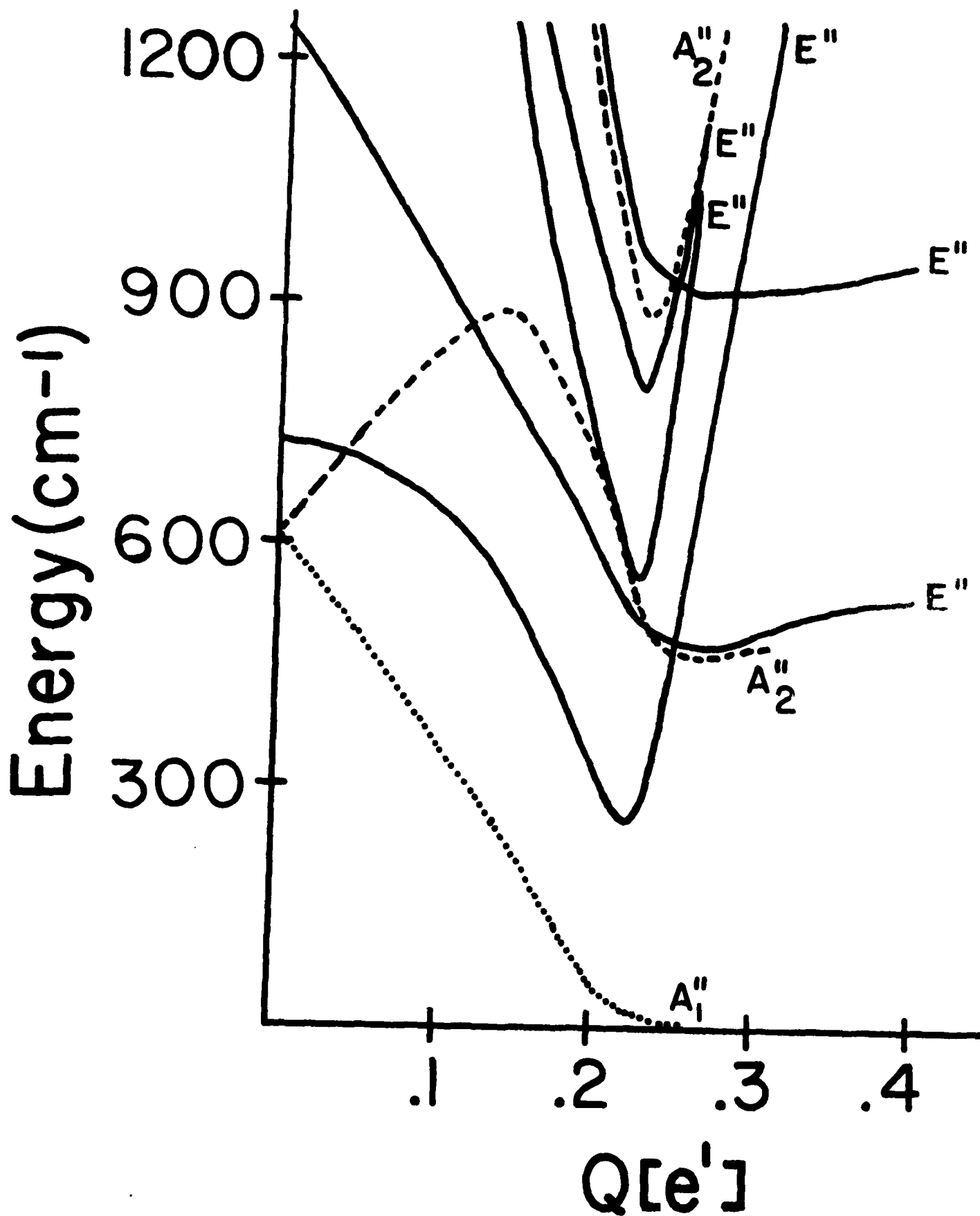


FIGURE 11

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